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(54) Title: UNLEADED MMT FUEL COMPOSITIONS			
(57) Abstract  Cold high energy fuel compositions for jet, turbine, diesel, fuel oil, and gasoline combustion systems. More particularly, relates to fuels comprised of enhanced combustion structure.			

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**UNLEADED MMT FUEL COMPOSITIONS****BACKGROUND OF THE INVENTION****5      Field of the Invention**

          This invention relates to fuel compositions for jet, turbine, diesel, and other combustion systems. More particularly, it relates to organomanganese fuel combinations, mechanical and/or chemical means capable of  
10      improving combustion, and/or reducing combustion temperatures, whereby thermal efficiency and hazardous emissions are improved.

**Description of the Prior Art**

15           The incorporation of various organo-manganese compounds as anti-knock agents (e.g. methylcyclopentadienyl manganese tricarbonyl -MMT, et al.) in hydrocarbon fuels is known. See U.S. Patents 2,818,417; 2,839,552; and 3,127,351 (incorporated herein by reference). Organo-  
20      manganese's use in heavier fuels such as coal, diesel and jet aviation fuels is also known and believed to help reduce smoke and solid particulate emissions. See U.S. Patents # 3,927,992; 4,240,802; 4,207,078; 4,240,801.

          Despite organo-manganese's anti-knock and other  
25      benefits, its use in hydrocarbon fuels produces another set of environmental and practical problems. Namely, organo-manganese compounds when combusted in hydrocarbon fuels generate harmful heavy manganese oxides ( $Mn_3O_4$  and  $Mn_2O_3$ ), which in turn coat engine parts, combustion systems,  
30      turbines, exhaust surfaces, emission/exhaust catalysts,

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etc., causing for example, early fatigue, failure, excessive wear, particulate emissions of metals, long term hydrocarbon emission degradation, and the like. See U.S. Patents 3,585,012; 3,442,631; 3,718,444; and my EPO Patent  
5 # 0235280.

For example, deposition of manganese oxide on jet engines, turbines, and the like, has long been a major obstacle to manganese's use. Due to the severity of these deposits, various methods were developed just to remove the  
10 oxides from jet engines. See U.S. Patent 3,556,846; 3,442,631; 3,526,545; 3,506,488. Unfortunately, due to the magnitude of this disability, manganese usage has been virtually halted in such applications.

It is also known that such deposits create a  
15 diffusional barrier on catalyst surfaces, which degrades catalytic efficiency. See Williamson, Gandhi, Weaver, "Effects of Fuel Additive MMT on Contaminant Retention and Catalyst Performance," SAE Paper 821193, 1982.

Thus, there was an extensive effort by Ethyl  
20 Corporation throughout the 1970's and 1980's to find a solution to this problem. Their effort included employing various oxygenated compounds in combination with organomanganese. See for example U.S. Patents Re. 29,488; 3,950,145; 3,948,618; 4,028,065; 4,052,171; 4,141,693;  
25 4,191,536; 4,317,657; 4,175,927; 4,082,517; 3,958,955; 3,926,581; and 3,926,580. However, there has was no successful commercialization of any technology solving this fundamental problem, despite overwhelming need.



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Thus, those skilled in the art have known for some time that organo-manganese, even at very low levels, causes the failure of U.S. regulated exhaust emission control systems, and that its use at any level is legally prohibited in unleaded gasolines within the U.S..

Even so, Ethyl Corporation's last failed effort to obtain an E.P.A. Waiver for MMT under § 211 (f) of the Clean Air Act was for a very modest manganese concentration of 1/32 gr (denied January 8, 1992).

All its prior efforts, including at manganese concentrations ranging from 1/64 to 1/8 gr, have resulted in failure. See generally Environmental Protection Agency RE Denial of Applications for MMT Waiver, Federal Register, Vol 43, No. 181, Monday September 18, 1978, and Ethyl Corporation; Denial of Application for Fuel Waiver; Summary of Decision, Federal Register, Vol. 46, No. 230, Tuesday, Dec. 1, 1981.

Recently, automotive manufacturers have raised renewed concerns regarding manganese's propensity to form deleterious oxides, that even at very low concentrations of 1/32 gram manganese, new onboard catalyst diagnostic systems known as "OBD-11 catalyst efficiency monitors" are impaired due oxide deposition on catalyst wash coat surfaces. See Hurley, Hansen, Guttridge, Gandhi, Hammerle, and Matso, "The Effect on Emissions and Emission Component Durability by the Fuel Additive Methylcyclopentadienyl Manganese Tricarbonyl (MMT)," SAE Paper 912437, 1991; Hurley et al, "Characterization of Automotive Catalysts

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Exposed to the Fuel Additive MMT," SAE Paper 890582, 1989; Hubbard et al, "Effect of MMT on the OBD-II Catalyst Monitor," SAE Paper 932855, 1993.

5 Thus, those skilled in the art, continuing to recognize MMT's long legal and environmental prohibitions, have generally abandoned the notion that manganese will ever be included in regulated unleaded gasolines and emission systems.

10 Even Ethyl Corporation (the sole manufacturer of MMT) for want of a real solution to abate or control adverse oxides, appears resigned to accept if an approval is ever to be granted, it will be for only very modest concentrations (e.g. up to 1/32 gr mn), and that catalyst coating even in these "small concentrations" is still a  
15 given. See Ethyl's last § 211 (f) Waiver Application and her EPO Applications 92302679.3; 91306359.0; 91306360.8; and 92307609.5. (filed concurrently with the Waiver effort).

20 The use of a broad class of fuel soluble carbonates is disclosed in the art. See U.S. Patent 2,331,386 (issued in 1939 prior to the present manganese oxide concern). This patent discloses a wide range of alkyl, homologous alkyl, aryl, and amide carbonated esters for use in oil furnaces and internal combustion engines.

25 Subsequent carbonate disclosure is found in the art and generally in the context of fuels or compositions that are metal/manganese free. For example, U.S. Patents # 4,891,049, 4,904,279 and 5,004,480 disclose metal free

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alkyl carbonates in middle distillate fuels for compression ignition, diesel, and jet engines.

U.S. Patent 4,600,408 (issued in 1986) discloses an alkyl phenyl carbonate as an anti-knock agent. This reference, noting the aforementioned organo-manganese oxide problem, likewise discloses the composition must be organo-manganese free.

Since those skilled in the art have long since abandoned hopes of solving organo-manganese's fundamental oxide disability, and given that manganese is only legal in U.S. leaded gasolines, practitioners have been disinclined to separate MMT from lead additive usage. See for example, European Patent Application 91306278.2 related to "Unsymmetrical dialkyl carbonate fuel additives," which apparently recognizes this reality by disclosing tetraethyl lead, tetramethyl lead and cyclopentadienyl tricarbonyl manganese together in the same context, absent suggestion of employing them independently of each other.

## Summary of Invention

Applicant has discovered a new class of high energy cool combustion compositions and processes.

The essence of Applicant's invention resides in the discovery of the source of heavy metal oxidation problem, namely the means to prevent heavy oxide generation during metallic combustion.

Applicant has discovered the operating mechanism causing fuels containing metallics, including

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organomanganese compounds to generate adverse heavy particulate/coating Mn oxides during combustion, which is namely caused by a less than ideal combustion process wherein combustion burning velocities and temperatures are not optimum.

By effectively increasing the burning velocity of the fuel, while ideally reducing combustion temperatures, Applicant not only controls or avoids the generation of adverse metallic oxides, but liberates the capacity of non-lead metallics to become principles in a new clean "high energy source" class of propellants/fuels and combustion process.

In essence Applicant has discovered a combustion process that comprises certain chemical structure/sub-structure and/or mechanical structure/sub-structure that simultaneously 1) increases burning velocity, 2) sustains a high release rate of what might be known as free energy, at 3) reduced combustion temperatures.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. Combustion Temperature Differences, compares differences in combustion temperatures of differing fuel compositions measured via exhaust gas temperatures at different engine loads.

Figure 2. Combustion Temperatures and Hydrocarbon Emissions, compares combustion temperature differences and their relationship to the generation of hydrocarbons emissions.

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Figure 3. **Combustion Temperatures and NOx Emissions**, compares combustion temperature differences and their relationship to the generation of NOx emissions.

Figure 4. **Indicated Burning Velocity**, compares the burning velocity of different fuels under differing loads.

Figure 5. **Burning Velocity and HC Emissions**, compares burning velocity to the generation of HC emissions.

Figure 6. **Burning Velocity and NOx Emissions**, compares burning velocity to the generation of NOx emissions.

Figure 7. **Technical Enleanment**, shows warm driveability and combustion improvements of gasoline due to maintaining minimum distillation temperatures for fuel containing oxygenated compounds.

#### DETAILED DESCRIPTION OF INVENTION

Applicant's discovery is discovery of the source of the heavy metallic oxide problem and its attendant solution, e.g increased burning velocity and/or reducing combustion temperatures, which is in essence the invention.

Applicant has discovered methods and compositions that accelerate and improve combustion to a more optimum state, while simultaneously reducing combustion temperatures and extending combustion interval.

Applicant has further discovered, under these improved combustion conditions, the metallic, itself, most unexpectedly becomes an integral and powerful agent in the combustion process, unexpectedly improving combustion

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thermal efficiencies, fuel economy, net available work, power generation, thrust, and the like, while simultaneously reducing hazardous pollutants.

5 In the context of this invention, Applicant generally refers to thermal efficiency, hereinafter, in both its chemical and mechanical context, e.g. the efficiency of the chemical reaction and the amount of useful work generated in the system, e.g. free energy.

10 Applicant has found in virtually every case, thermal efficiency, particularly as measured as a function of net useful work generated by the system is increased. Often very substantially. Simultaneously, due to the cool nature of the combustion temperatures, combustion systems will enjoy extended useful life, and ease of operation, as heavy  
15 oxides are not formed.

For example, Applicant's has unexpectedly discovered thermal efficiency over existing fuels and combustion systems to be on the order of 2.0% to 20%. And, depending upon the circumstances (e.g. combustion systems, fuel  
20 configurations) average improvements can range from 2.0% to 5.0%, 5.0% to 10.0% or higher, with modest improvements ranging from 0.05% to 1.0% to 2.0%. Exceptional improvements will range from 10%, 25% to 40%, 30% to 80%, or more.

25 Additionally, Applicant ultimately expects additional improvements on the order of 5% to 25%, or more, due to modifications of combustion and fuel injection systems

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designed to optimize the unique combustion features of Applicant's invention.

Applicant expects significant combustion and energy conversion improvements at altitude in the case of aviation jet systems, aviation gasoline engines. Similar improvements are contemplated for a wide range of applications, e.g. diesel, gasoline, fuel oils, gas oil turbines, etc.

Applicant's combustion methods, fuel chemistry, combustors, fuel injection system, air breathing and emission system are critical structure to the practice of this invention.

Applicant has found unexpected synergism and multiple advantage that will become evident in employing this invention, as will become more fully described below.

Thus, novel design, method, and/or operation of an engine, a combustor, combustion system, injection, air-breathing and/or emission systems, enhancing the combustion object of Applicant's invention are express embodiments.

The simultaneous operation of one or more said systems, or the independent employment of a single system, or component or sub-component of said system, is contemplated in the practice of this invention. Further, it is an embodiment such structure may be employed independently of Applicant's enhanced combustion fuels, which are independently capable of achieving enhanced burning velocity and/or reduced combustion temperatures.

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However, the coupling of the systems achieves synergism, which could not otherwise be achieved.

The invention fundamentally resides in increasing 1) burning velocity by a) increasing laminar burning velocity  
5 (ECS chemical and/or distillation modification means), b) increasing turbulent velocity (chemical and/or mechanical means), 2) reducing combustion temperature (chemical or mechanical means), in combination with a metallic component based fuel.

10 Thus, applicant's invention incorporates multiple interrelating chemical and mechanical elements, all vital to the practice of the invention.

It is an embodiment of this invention to employ any number of non-lead metallics (cyclomatic manganese  
15 compounds however are initially preferred), as a component of Applicant's fuel composition.

However, metallic use is not required, as will become evident below. Thus, in the disclosure below it is expressly contemplated disclosure of a metal may be read in  
20 the alternative.

It is contemplated that compounds/components and/or chemical and/or mechanical, processes, methods and means, including combinations and subcombinations thereof, which increase combustion burning velocity be employed. It is  
25 preferred that, while not required, that combustion temperatures be simultaneously reduced.

In the practice of the invention, should an oxygenated compound be employed, maximizing oxygen is a desire. Oxygen



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contents may range from 0.0001 to 80.0% by weight. Individual fuel composition and combustion systems dictate. However, beneficial results do not tend to occur until 1.0%, 1.5%, 2.0% or more oxygen is included. More preferred concentrations are 2.0% or more. However, smaller concentrations are acceptable in co-fuel applications. A desirable range is from 0.001 to 30.0% oxygen by weight. Additional weight concentrations of oxygen include 0.001 to 15.0%, 0.5% to 1.5%, 0.3% to 2.7%, 2.0% to 3.7%, 0.2% to 0.9%, 1.0% to 4%, 2.0% to 8.0%, 1.8% to 12%, 2.0% to 10.0%, 3.0%, 5.0% to 40%, 2.0% to 53%

It is anticipated in neat fuel and rocket applications, oxygen concentrations will be significant. In initial co-fuel applications (see below) concentrations will be more modest. However, it is an object to include significant concentrations of oxygen in Applicant's fuels, especially reactive oxygen, which can quickly and aggressively react with the metallic.

In the practice of this invention, acceptable increases in the rate of the fuel's burning velocity over an unadjusted fuel or combustion system will range from 1.0% to approximately 800%, or more. Velocity increases of 0.2%, 0.5%, 1.0%, 2.0%, 3.5%, 5% to 10.0%, 7.0% to 15%, 9.0% to 25%, 5.0% to 20%, 12% to 30%, 15% to 40%, 20% to 50% are desirable. More desirable increases range from 5% to 60%, 10% to 80%, 20% to 100%, 30% to 150%. Other increases are from about 100% to 200%, 100% to 300%. Increases of 200% to 400%, 300% to 600%, 400% to 800%, 500%

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to 900% are also contemplated and desireable. Increases of 300%, or more, are highly desireable, especially in Applicant's advance fuel and combustion systems. Increases outside these ranges are contemplated and desireable.

5 Differing chemical means will also influence differing burning velocity increases, and fuel application. It is an express object of this invention to optimize burning velocities in light of the fuel chemistry, combustion systems, fuel injection and air breathing systems,  
10 operating conditions, desired thermal efficiency, and cost.

Burning velocity increases and/or combustion temperatures reductions will vary depending upon the modifications to fuel compositions, combustion and mechanical systems.

15 It is expressly contemplated that compression ratios, compression pressures, combustion pressures, combustion chamber design, temperature of unburned gas compositions, equivalence ratios, ignition timing, residual gas fractions, fuel injection pressures and timing, air  
20 breathing systems, air input temperatures, exhaust systems, exhaust catalysts, heat exchange method/systems, lubrication systems, coolant systems, and/or related methods and/or devices, including combinations and/or subcombinations thereof, will be modified to beneficially  
25 take advantage of, enhance, or otherwise make possible the improvements in burning velocities and/or reduction in combustion temperatures.

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It is anticipated that knock sensor technology may be employed in higher compression spark ignited engines, operating on gasoline, as necessary to control spark timing to avoid knock. Thus, it is contemplated that Applicant's preferred higher compression ratio engines will simultaneous employ knock sensor technology.

It is contemplated that many applications of the invention will not be fully appreciated until certain thresholds of operation are achieved. For example, and as will be set forth in more detail below, the benefits of improved fuel economies may not fully appear until the engine is operated under moderate to moderately heavy load conditions. Furthermore, absent other adjustments mechanical modification, e.g. reductions in MBT spark advances for gasolines, etc., the full benefit of the invention can not be enjoyed.

Increases in the pre-ignition or post-ignition partial pressure of the vaporized fraction is particularly effective in influencing improvements in burning velocity. Thus, the character of the pre-ignition/post-ignition vaporized fraction and those features related to the diffusion of heat and active reaction centers in unburned gases, and the like, are determinative and are intended to be optimized as an object of this invention.

It is an object of Applicant's invention that the diffusion of pre/post ignition pre-combustion gases operate to increase the momentum/viscosity of the unburned gas to as close as possible to the viscosity of the burned gas, in

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order to reduce the viscous drag between the burned and the unburned gases. It is in the elimination of this drag, which the principal object of increases in burning velocity are achieved.

5           Thus, evaporation or injection or compression of the unburned fuel vapor fraction, in a such a manner, to increase its partial (vapor) pressure as gaseous mixture, prior to its combustion is desireable and contemplated.

10           Further, compounds/components and/or mechanical and/or other means that increase the temperature, velocity of the gaseous mixture within the combustion chamber post ignition/pre-combustion are preferred.

15           In the vapor state, fuel density differences of a given fuel do not necessarily directly influence improvements of burning velocity. In other words, burning velocity improvements of Applicant's invention do not appear necessarily sensitive to fuel type, once vaporized and/or once injected into the chamber/combustor in the manner and in the desired particle sizes contemplated by  
20           this invention.

          Thus, compositional changes in the vapor fraction, due to changes in partial vaporization does not, in itself, necessarily produce measurable effect.

25           The rate of flame propagation relative to unburned gas, in practical fuel-air-residual gas mixtures is a fundamental parameter that directly influences the invention's beneficial objects. Thus, maximizing the elementary reactions that take place in the flame and

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adapting the mass and thermal diffusivity of the various gaseous species comprising the composition of enhanced combustion (see below), to yield increased combustion burning velocity, is an express embodiment of this invention.

As noted, it is an object to increase turbulent burning velocity, which is both a function of thermodynamic and turbulent parameters. Turbulence is related to engine design, combustion chamber design, fuel injection operation and engine operating parameters, such as equivalence ratio and spark timing.

It is an express embodiment of this invention to increase turbulent burning velocity by increasing laminar burning velocity, as increases in laminar are compounded in turbulent velocities.

It is an embodiment to increase laminar burning velocity by modifying thermodynamic factors, including but not limited to improving the thermal, diffusion, fuel chain branch characteristics of the fuel's composition enhancement chemistry, modifying distillation temperature, modifying ECS chemistry (see below), modifying fuel equivalency ratios, modifying spark advance, reducing injected fuel particle sizing, modifying injection angles, pressures, compression pressures, and improving air-breathing capability, and the like.

It is an embodiment to increase turbulence by modifications in shape and design of combustion system, combustor, combustion chamber and/or also from the velocity

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and/or direction of the gases flowing into the combustion chamber, before, during, and after combustion, e.g. pre-combustion chambers.

Those means that operate to increase combustion pressures and/or compression pressure are also desirable.

In the case of a spark ignited internal combustion engine, flame velocity is also proportional to intake velocity. However excessive intake velocities can materially reduce the weight of the fuel and air charge taken into the cylinder. To obtain high turbulence without high intake velocities, combustion chamber designs, which produce turbulence near the end of the compression stroke are desirable. Turbulent pre-combustion chambers, advanced fuel-air mixing systems and other means are preferred.

However, it is an embodiment of this invention to employ high intake velocities to increase turbulence, because ECS chemistry is able to materially offset reductions in charge weight. Thus, turbo-charging and super-charging are express embodiments and are preferred.

It is expressly contemplated that combustion systems, which have a lower relative octane number requirements (ONR), or which require lower compression ratio's, or which permit the use of a higher compression ratio on fuels of a given octane number, be employed.

Chemical and/or mechanical means, including for example, exhaust oxygen sensing systems (including EGO sensors) that adjust fuel-air equivalency ratios, which

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enhance the burning velocity object of this invention, are desirable and contemplated.

As will be evident that many chemical and mechanical means, and variations exist, which when combined and  
5 utilized in accord with Applicant invention, accomplish the objects of this invention.

#### BOILING TEMPERATURE REDUCTION AND MODIFICATION PRACTICE

Additional means of reducing combustion temperatures  
10 and improving burning velocities are contemplated. One such means is by reducing the end boiling point of the composition. Applicant has discovered that by reducing or eliminating higher boiling point hydrocarbons from the fuel, the fuel's average latent heat of vaporization is  
15 increased absent loss of work potential. Applicant has unexpectedly discovered that fuel economy improvements.

It is Applicant's intent that reduction and/or modification of hydrocarbon co-fuel's T-90, T-50, or T-10 distillation be modifying underlying hydrocarbons streams,  
20 or tailoring.

Thus, by reducing boiling temperatures, e.g. end boiling and T-90 temperatures, in combination with Applicant's invention, combustion temperatures and/or burning velocity is improved.

25 Wide boiling fuels benefit from end boiling, T-90 boiling and T-50 reductions including gasolines, gas oil turbine fuels, fuel oils, diesel fuels, and automotive



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gasolines. Limited application applies to narrower boiling fuels.

For example, in wide boiling petroleum fractions, e.g. diesel, heavy diesel, gas oil turbine fuels, wide cut jet fuels (Jet B, JP 4), fuel oils, gasolines, etc., reducing the fuel's distillation boiling temperatures, especially end point and/or T 90 temperature by 5<sup>0</sup>F to 20<sup>0</sup>F, 10<sup>0</sup>F to 30<sup>0</sup>F, 20<sup>0</sup>F to 50<sup>0</sup>F, 25<sup>0</sup>F to 60<sup>0</sup>F, 40<sup>0</sup>F to 70<sup>0</sup>F, 50<sup>0</sup>F to 80<sup>0</sup>F, 60<sup>0</sup>F to 90<sup>0</sup>F, 70<sup>0</sup>F to 100<sup>0</sup>F, 80<sup>0</sup>F to 120<sup>0</sup>F, 40<sup>0</sup>F to 150<sup>0</sup>F, 75<sup>0</sup>F to 175<sup>0</sup>F, 60<sup>0</sup>F to 200<sup>0</sup>F, 70<sup>0</sup>F to 225<sup>0</sup>F, 80<sup>0</sup>F to 250<sup>0</sup>F, 90<sup>0</sup>F to 275<sup>0</sup>F, 100<sup>0</sup>F to 280<sup>0</sup>F, 110<sup>0</sup>F to 300<sup>0</sup>F, 120<sup>0</sup>F to 320<sup>0</sup>F, 140<sup>0</sup>F to 350<sup>0</sup>F, or more, is particularly effective in increasing the fuel's inherent latent heat of vaporization, reducing combustion temperatures, and increasing combustion burning velocities, etc.

Thus, it is a specific embodiment of this invention to reduce end point and T-90 boiling temperatures of co-fuels, which are used together with ECS fuels and or as stand alone fuels.

It is also an embodiment to reduce T-50, T-10 temperature in such a manner to improve combustion.

In the practice of this invention end point/T-90 reduction is contemplated with metallic use, absent ECS compound; whereby reductions in the formation of free carbon in primary combustor zones, reductions in hazardous exhaust emissions, reductions or control of manganese oxides on exhaust catalyst beds, and the like, occur. In



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the case of automotive fuels, this T-90 reduction tends to reduce VOC, hydrocarbon and/or NOx emissions.

Quite unexpectedly, Applicant has discovered that when reducing gasoline t-90 temperatures to less than 270°F, a material combustion advantage occurs in combination with minor amounts of Mn. Applicant has discovered that fuel economy and/or mileage unexpectedly improved, even though higher heating value components had been eliminated in the T-90 reduction.

Obviously, this effect is sensitive to the fuel and the components that are eliminated and those that remain after T-90 reduction.

#### Example 1

A method of increasing the fuel economy of a vehicle operating on convention or reformulated gasoline comprising: Reducing the boiling temperature of gasoline such that its boiling temperature at T-90 fraction is no greater than 270°F; mixing MMT into the composition up to 1/32 gr mn/gal; combusting said composition in a gasoline powered vehicle; whereby fuel economy is improved by 0.5% or more.

#### Example 2

The method of example 1, wherein fuel economy is improved over the clear fuel not having reduced T-90 temperatures and same fuel containing MMT.

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Preferred boiling point practice reduction includes the elimination of higher boiling point alkanes, aromatic hydrocarbons, cyclanes, alkenes are preferred.

5 Similar reductions and/or control of T 50 temperatures are also desireable, so long as technical enleanment or warm driveability is not impaired.

Applicant notes, mid range boiling point control is particularly important in fuel application where oxygenates are employed, especially in carburetor systems.

10 In the practice of this invention, said boiling point modification/control, enhances combustion and/or the burning velocity features of the fuel.

When an oxygenated compound is employed in excess of 0.5% by weight oxygen content in the fuel, especially for  
15 operation in current engines, mid-range temperatures should be from about 160°F/170°F/180°F to about 205°F. Mid range temperatures outside these ranges appear to be less effective.

Importantly, Applicant has discovered when employing  
20 both T-90 temperature reduction and mid-range temperature control, the Mn fuel (absent the inclusion of an oxygenate) achieves maximum combustion advantage, e.g. improved fuel economy, reduced manganese oxide formation, and/or improved warm driveability.

25 Furthermore, the inclusion of an oxygenate enhances this beneficial effect. The better the ECS oxygenated compound the better the beneficial result.

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Applicant appreciates that automotive engines and fuels will be modified in the future to achieve even better performance and emission results, accordingly, Applicant contemplates even lower T-90 and mid-range boiling temperatures in future applications.

#### Example 3

A fuel composition wherein the reduction of end boiling point and/or T-90 temperatures operates to increase average latent heat of vaporization.

#### Example 4

The example of 3, wherein combustion emissions or fuel economy of a manganese fuel having reduced T-90 temperatures of 270°F, or less, are improved compared same fuel unadjusted for T-90 temperatures.

#### Example 5

The example of 4, wherein fuel T-90 temperature is less than 280°F, more preferably less than 270°F, and MMT is included in the amount of 1/32 gr. Mn/gal, wherein fuel economy over same unadjusted fuel is greater than 0.2%.

#### Example 6

The composition of example 5, wherein reduced emissions include toxic and/or NOx emissions.

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Example 7

The example of 5, wherein MMT is contained in a quality of 1/32 gram mn or less, per gallon, and wherein fuel economy is improved by 0.2% (1.0%, 1.5% or more preferred).

Example 8

The example of 7, where an oxygenated ECS compound is employed in excess of 0.5% by weight for operation in current automotive engine, and wherein the gasoline's mid-range temperature is from 170°F to approximately 205°F.

Example 9

The example of 8, wherein the composition comprises an ECS compound in a sufficient concentration to increase average burning velocity of composition by an additional 5.0%, or more, over clear composition as measured by laminar bunsen burner.

Example 10

The example of 9, wherein the addition of the ECS compound is sufficient to reduce average combustion temperatures by 25°F, as measured under load of at least 20 indicated horse power (ihp).

Applicant notes this aspect of his invention (e.g. addition of ECS compound with/or without metallic) as applied to gasoline is especially beneficial when T-90 temperatures are equal to or below approximately 300°F,

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280°F, 270°F, 260°F, and optionally when T-50 temperatures are in the range of approximately 160°F to 205°F or 170°F to 205, 180°F to 205°F; or alternative 160°F to 190°F or 160°F to 180°F (particularly in later date applications).

5           The application of mid-range temperature control is generally applicable to all wide boiling fuels.

#### COMBUSTION TEMPERATURE MODIFICATION

10           In the practice of this invention, preferred reductions in combustion temperatures range from 10°F to 500°F. Reductions of 25°F to 50°F, or more, are desireable. Reductions of 100°F, or more, are desireable. Reductions of 5°F to 15°F, 10°F to 25°F, 15°F to 30°F, 20°F to 40°F, 25°F to 45°F, 30°F to 50°F, 35°F to 60°F, 40°F to 55°F, 45°F to 60°F, 15 50°F to 65°F, 55°F to 75°F, 65°F to 75°F, 70°F to 95°F, 85°F to 105°F, 100°F to 120°F, 110°F to 140°F, 100°F to 130°F, 110°F to 150°F, 120°F to 160°F, 150°F to 250°F, 250°F to 450°F, 200°F to 500°F, 300°F to 600°F, 200°F to 800°F, 400°F to 1000°F, 300°F to 900°F, 500°F to 2000°F, 600°F to 2500°F, or more, are 20 preferred, especially with simultaneous increases in burning velocity. Reductions outside above ranges are fully expected, especially as the concentration of the Applicant's enhancement combustion compounds (see below) increase as a percent volume of the fuel composition.

25           In the case of gasoline, reduced exhaust temperature translates into increased power and/or reductions of exhaust catalyst inlet temperatures. It is an express embodiment of this invention that exhaust catalyst inlet

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temperatures be reduced to avoid catalyst plugging. Hence it is an express object to reduce catalyst inlet temperatures to about 1400°F or less, 1350°F, 1300°F, 1250°F, 1200°F, 1150°F, 1100°F, 1050°F, or less, other temperature  
5 sufficient to assure acceptable catalyst activity while avoiding the likely hood of manganese oxide plugging.

This feature is also contemplated even when low concentrations of metal are included in the fuel. As noted, at modest levels of up to 1/32 gram Mn, there is undisputed  
10 evidence that wash coat surfaces are coated with minor amounts of manganese oxides. This minor Mn coating operates to store oxygen and creates a false impression to a downstream oxygen sensor (known as an OBD-II catalyst efficiency monitor) designed to look for the lack of oxygen  
15 in post catalyst exhaust gases. Unfortunately, the manganese deposits, by storing oxygen from exhaust gases, operates to mask the catalyst's true efficiency. In other words, the OBD will show a defective catalyst's efficiency as being acceptable due to manganese's oxygen storage  
20 capacity. Thus, the manganese coating action additionally causes the failure of OBD monitors.

Thus, combustion temperature control, absent any other aspect of Applicant's invention, is contemplated as a means of control wash coat deposits from low mn concentrations.

25

#### Example 11

A method of avoiding the plugging or coating of exhaust catalysts with manganese oxides, said method

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comprising: mixing an ECS fuel of high latent heat of vaporization in sufficient quantity with a conventional unleaded or reformulated gasoline containing 1/32 gr or more Mn/gal of MMT, wherein said fuel's combustion and exhaust temperatures are sufficiently reduced that inlet exhaust gas temperature of catalyst is less than 1400°f, more preferably less than 1200°F.

#### Example 12

A method of avoiding the plugging or coating of exhaust catalysts with manganese oxides, said method comprising: modifying T-90 gasoline temperatures to reduce combustion temperature of a low mn containing fuel, wherein said fuel's combustion and exhaust temperatures are sufficiently reduced that inlet exhaust gas temperature of catalyst is less than 1400°f.

Applicant has found temperature reductions to be more significant in higher temperature systems.

#### Example 13

In combination, a fuel, a combustion system, the combination characterized by: said combustion system combusting said fuel containing a combustion improving amount of CMT, and chemical means for reducing combustion temperatures and simultaneously increasing burning velocity, whereby combustion temperatures are reduced by at least 10°F 25°F 50°F and combustion burning velocity is increased by at least 10%, such that fuel economy under a

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load varying from 14 ihp to 24 ihp increased by at least 5.0%. (Example is supported directly from test data reflected in Figures 1 and 4, where actual reduction in temperature approached 72°F and fuel economy increased 20% to 30%)

#### Example 14

The combination of example 13, wherein the temperature reducing and burning velocity means is dimethyl carbonate and the metal concentration ranges from 0.01 to 3/16 gr Mn/gal of MMT.

#### **CHEMICAL MEANS**

It has been unexpectedly discovered that certain molecular features of combustion are responsible for the rapid diffusion of heat and active reaction centers in unburned gases, including the rapid diffusion of unburned gases in front of the flame front, resulting in increased burning velocities. Such molecular structure includes, but is not limited to H, H<sub>2</sub>, O, O<sub>2</sub>, CO, F, F<sub>2</sub>, F<sub>3</sub>, N, B, Be, BO, B<sub>2</sub>, BF, AL ALO, CH<sub>3</sub>, NH<sub>3</sub>, CH, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>, Li, ONH, NH, NH<sub>2</sub>, OCH<sub>3</sub> (methoxy radicals), OCH, OCH<sub>2</sub>, and OH (hydroxyl radicals). Additional chemical structure believed capable of achieving beneficial results include Cl, OCOO, COOH, C<sub>2</sub>H<sub>5</sub>OOC, CH<sub>3</sub>CO, OCH<sub>2</sub>O, OCHCO, and CONH<sub>2</sub>.

It is preferred that these radicals during combustion are unstable having a free or unused valency electron that can chemically bond. It is highly desireable that they act



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as chain carriers in the main chain reaction of combustion, particularly in combination with a metallic. Combustion yielding dissociated and unstable molecules and atoms (e.g. OH, CN, CH, NH, etc.) with subsequent reassociation, leading to continuing combustion, increasing exhaust velocity, is preferred.

Applicant has found the heat of formation of his preferred free radicals is relatively low. Acceptable heats of formation for said free radicals typically are less than 150, 100, 75, or 50 K cal mole<sup>-1</sup>. Other heats of formation include 34 (CH3), 26 (C2H5), 9.3 (OH), 2.0 (CH3O) Kcal mole<sup>-1</sup>. It is contemplated that negative heats of formation are also acceptable.

A positive or low negative heat of formation for the chemical compound containing said free radicals (ECS compound) is preferred. Acceptable negative ranges include those less than approximately -200, -180, -160, -150, -145, -130, -120, -100 Kcal/mol, with more preferred being less than -90, -80, -75, -70, -65 Kcal/mol and the most preferred being less than approximately -60, -55, -50, -45, -40, -35, -30, -20, -10 kcal/mol, or positive in value. The closer to a positive or the higher the positive, the more preferred.

Those ECS compounds, which easily decompose and/or dissociate generating significant free radicals in compression, early and/or regular ignition or combustion, are desirable. It is desirable that dissociation occurs below normal or normal combustion, compression, or at or

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near ignition temperatures (unless pre-ignition is a concern). It is desirable that dissociation acts to quickly diffuse unburned vapors in front of the flame front, whereby burning velocity is increased.

5           It also is particularly desirable that this structure and/or the ECS compound have high latent heats of vaporization (enthalpy of vaporization), particularly those equal to or greater than  $28.0 \text{ kJ mole}^{-1}$ . Other enthalpies of vaporization (at the boiling point) are those equal to or  
10 greater than 21, 22, 24, 26, 27, 30, 32, 34, 36, 38, 40, 42, 43, 45, or more  $\text{kJ mole}^{-1}$ . Generally, the higher the better.

Preferred latent heats of vaporization at  $60^\circ\text{F}$  are those equal to or greater than 75, 100, 140, 150, 160, 200,  
15 250, 300, 350, 400, 450, 500  $\text{btu/lb}$ , or more. It is generally preferred that the latent heat of vaporization of the ECS compound be at least the same as, more preferably 5.0%, 10%, 25%, 50%, 75%, 100%, 150%, 200%, 250%, 300%, or greater, than any base or co-fuel to which the compound  
20 might added. Normally, the higher the better.

Applicant has discovered, the higher the relative difference, the higher, for example, intake charges can be cooled and the greater the improvements in volumetric efficiency.

25           The molecular structure yielding high latent heat and/or accelerated burning velocity, etc., to wit, that structure causing the immediate high kinetic diffusion of the unburnt combustion vapor, etc., and/or otherwise acting

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in the combustion process to increase burning velocity (and exhaust velocity), and/or reduce combustion (and/or exhaust) temperatures is hereinafter referred to as "Enhanced Combustion Structure or ECS." Those compounds which contain such structure are referred to as ECS compounds.

It is preferred that ECS compounds rapidly decompose at temperatures slightly to moderately higher than ignition temperatures but below combustion temperatures. While decomposition at higher or even lower temperatures is contemplated, including those below ignition temperatures. However, in the case of gasolines pre-ignition should be avoided. It preferred that ECS compounds be thermally stable in normal handling and operating temperatures up to approximately 150°F-300°F, but readily decomposes at approximately temperatures approaching 300°F to 800°F, 300°F to 500°F, more preferably at 400°F to 500°F. However, decomposition at temperatures outside of these and/or may occur for example during injection, compression, or prior to ignition, after ignition, and/or combustion.

Preferred fuel chain characteristics of Applicant's organic ECS compounds are those containing limited number of carbon atoms in chain with 3 or few atoms preferred. 2 carbon atoms or single carbon are highly preferred.

Non-limiting examples of compounds that Applicant has identified that contain ECS structure and that are likely to be effective in accomplishing this object, include: hydrogen, carbon monoxide, methylene di methyl ether (also

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known as methylal, dimethoxy methane), carbonic acid dimethyl ester (also known as dimethyl carbonate), diethyl carbonate, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), methyl tertiary amyl ether, methanol, ethanol, propanol, tertiary butyl alcohol, dimethyl ether, other C<sub>3</sub> to C<sub>6</sub> lower molecular weight alcohols, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, dimethyl ether diethyl ether, isopropyl ether, diisopropyl, nitromethane, nitroethane, nitropropane, nitrous oxide, dinitrous oxide, nitric oxide, ozone, water, gas hydrates (methane hydrate), hydrogen peroxide, and similar compounds. Applicant believes many other ECS compounds exist, that have not yet been identified.

Such compounds, hereinafter, are referred to as "ECS Compounds" because they contain ECS structure and/or have the capacity during the vaporization/compression/combustion/exhaust process cause the generation of said ECS structure.

Applicant acknowledges there is great variability in performance and characteristics between ECS compounds, and that in certain neat and/or co-fuel applications, certain ECS compounds may be less satisfactory than others, or altogether unsatisfactory. Several, for example, may be very effective in non-regulated aviation, advanced jet applications, diesel applications, but unacceptable for automotive purposes. It is recognized that differing ECS compounds will elicit differing response in same fuel and/

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or combustion system. For example, it is expected that in certain applications alcohols will elicit lower combustion and exhaust temperatures than ethers, due to differences in latent heats of evaporation.

5 ECS compounds may be solids, liquids, gases, and mixture, and may be selected from alcohols, amines, esters, di-esters, glycols, ethers, aldehydes, ketones, glycols, glycol ethers, peroxides, phenols, carbonxylic acids, nitrates, di-nitrates, carbonates, di-carbonates, and the  
10 like.

ECS compounds may be ethers, esters, amines, and/or other compounds containing carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, ethoxalyl, glyoxylyl, methoxy, methylenedioxy, glycolyl, and/or hydroxyl components and/or  
15 radicals.

Additional non-limiting examples of ECS compounds include ethylene, propylene, tertiary butylcumyl peroxide, butylene, 1,2-butadiene, 1, 3-butadiene, actetylene hydrocarbons including acetylene, allylene, butine-1, pentine-1, hexine-1; substituted hydrazines, including  
20 methylhydrazine, symmetrical dimethylhydrazine, unsymmetrical dimethylhydrazine, hydrazine; ethane, propane, butane, diborane, tetraborane, penta bornane, hexaborane, decaborane, aluminum borohydride, beryllium borohydride, lithium borohydride, ammonium nitrate, potassium nitrate,  
25 nitric acid, ammonium azide, ammonium perchlorate, lithium perchlorate, potassium perchlorate, nitrogen trioxide, nitrogen dioxide, hydrazoic acid, dicyanogen, hydrocyanic

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acid, monethylanile, acetylene, aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, diborane, dimethylamine, diethylenetriamine, ethanol, ethylamine, ethylene diamine, ethylene oxide, ethylenediamine, ethyl  
5 nitrate, dimethyl sulfide, furfuryl alcohol, heptene, hydrazine, hydrogen, isoethyl nitrate, isopropyl alcohol, lithium, lithium hydride, methane, methylal, methanol, methyl nitrate, methylamine, methylacetylene, methylvinyl acetylene, monoethylaniline, nitromethane, nitropropane,  
10 nitroglycerine, n-octane, propane, propylene oxide, n-propyl nitrate, o-toluidine, triethylamine, trimethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, xylidine, 2,3-xylidine, lithium borohydride, monomethylhydrazine, pentaborane, and the  
15 like. Other chemistry Applicant has identified as likely candidates include  $\text{OHC}(\text{CH}_2)_4\text{CHO}$ ;  $\text{CH}_3\text{CHOHCHOHCH}_3$ ;  $(\text{CH}_3)_3\text{CCHOHCH}_3$ ;  $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_3$ ;  $(\text{CH}_3)_2\text{COOH}$ ;  $\text{CH}_3\text{CCCOH}$ ;  $(\text{CH}_3)_3\text{CCH}_2\text{COH}$ ;  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ;  $\text{HOCH}_2\text{CH}_2\text{OH}$ ;  $\text{OCH}_2\text{CHCHO}$ ;  $(\text{CH}_3)_3\text{CCHO}$ ;  $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_3$ ;  $\text{C}_5\text{H}_4\text{O}_2$ ;  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ ;  
20  $\text{C}_3\text{H}_7\text{COCO}_2\text{H}$ ;  $\text{C}_5\text{H}_8\text{O}_2$ , and others.

It is additionally contemplated that certain ECS compounds will be co-ECS compounds and required the assistance of one of more ECS compounds and/or require mechanical structure to either satisfactorily enhance  
25 burning velocity and/or to reduce combustion temperatures. For example, it may necessary to reduce combustion temperatures of certain high velocity ECS compounds by admixing an alcohol, carbonate and/or admixing water for

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example by separate injection. It is expected that certain synergies exist between ECS compound, likely to enhance each's capability.

Another feature of Applicant's ECS compounds is their superior flame propagation velocity features. As a rule, when combusted in air (as a function of their own constitution and as measured in a laminar Bunsen flame), flame velocities should be equal to or greater than 40, 43, 45, 48, 50, 60, 65, 70, 75, 80, 90, 100, 110, 120, 130, 140, 150 cm/sec. Flame velocities of ECS compounds herein may be measured independently or in the presence of a preferred metallic. Flame velocities of ECS compounds in the presence of a metallic are generally expected to be greater, than absent said metallic.

Generally, preferred laminar flame propagation velocities should exceed 55 cm/sec. The higher the better. It is preferred that the flame velocity of an any ECS compound as measured in laminar bunsen flame be at least .05% to 1.5%, 1.0% to 3.0%, 2.0% to 4.0%, 3.0% to 6.0%, 5% to 10%, 7% to 20%, 8.0% to 30.0%, 10% to 40%, 15% to 60%, 30% to 200%, 50% to 300%, or more, than a co-fuel.

#### Example 15

A post-ignition, pre-combustion composition containing a diffusion increasing amount of ECS, whereby combustion burning velocity is increased.



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Example 16

A pre-ignition vapor composition containing a diffusion increasing amount of ECS, whereby a minimum flame propagation of 60 cm/sec is achieved by a maximum spark  
5 energy of 0.2 mJ, preferably 0.15, 0.10 or less mJ.

Example 17

The vapor composition of examples 15 and 16, wherein the diffusion increasing ECS vapor is derived from the  
10 decomposition product of dimethyl carbonate.

Example 18

The composition of examples 15 and 16, wherein the composition is a combustion composition.

15 Thus, those elements, ECS compound/components wherein the above enhanced combustion structure exist, in high relative concentrations and/or which become intermediate and/or initial/pre-combustion and/or combustion  
structure/product, especially in the vapor charge and/or in  
20 the vapor of compression and/or combustion, and which causes rapid diffusion of the flame front, and/or rapid diffusion of uncombusted vapors and/or otherwise accelerates and/or improves combustion are most preferred.

The higher the relative volume of enhanced combustion  
25 structure as a percent of the volume of uncombusted vapor fraction, the better.

Thus, it is an embodiment of this invention to employ a sufficient amount of enhanced combustion structure in the



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vapor fraction to increase the rate of diffusion. It is contemplated that the diffusion means of Applicant invention additionally incorporate separate laminar and/or turbulent burning velocity increasing means.

5 ECS compounds preferably should be soluble in the fuel composition to which it is added. However, dispersants or other means, including mutual solvents, may be employed. Alternatively, insoluble or partially soluble ECS compounds may be employed in emulsions and/or by other means,  
10 including by separate injection, and/or by hybrid means.

It is contemplated in the practice of this invention ECS compounds need not contain ECS structure, if their use or combination otherwise generates or causes to be generated ECS structure in the compression, ignition and/or  
15 combustion process. Thus, in the practice of this invention a compound, which enhances the formation of ECS in the combustion process is deemed to be an ECS compound.

Higher octane oxygenated ECS compounds tend to improve ignition quality. ECS compounds with higher latent heats of  
20 evaporation, which reduce compression, post ignition (pre-ignition) and/or reduce combustion temperatures, are particularly preferred.

Emulsions or other combination, including those containing ECS, are also desirable, particularly those  
25 capable of causing vapor fraction droplets to explode or to explode outside the spray or to otherwise cause quick diffusion of the vapor fraction. Such non-limiting ECS

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emulsion compounds include water, methanol, hydrogen peroxide, rape seed oil, and the like.

Preferred ECS compounds should be relatively simple in molecular structure. In the case of liquid fuels, ECS compounds that do not adversely increase the vapor pressure or flash point of the base fuel at ambient or operating temperatures are more preferred. Acceptable blending vapor pressures range from 0.5 to about 50.0 psi. More desirable blending vapor pressures range from 0.5 to 15.0, 0.5 to 12.0, 0.5 to 10.0, 0.5 to 9.0, 0.5 to 8.0, 0.5 to 7.0 psi, or 0.5 to 6.0 psi, or 0.5 to 5.0 psi, or from 0.5 to 3.0 psi, or less. Individual vapor pressure ranges include 5.4, 5.6, 5.7, 5.9, 6.1, 6.3, 6.6, 6.8, 6.9, 7.1, 7.2, 7.5, 7.6, 7.7, 8.1, 8.3 psi.

It is preferred that ECS compounds employed directly (as opposed to for example separate injection) in liquid fuels do not adversely increase the flash point of the base fuel. ECS compounds having boiling points in excess of 50°F are acceptable. Those above 80°F are desirable. However, boiling points in excess of 90°F to 150°F, or even 200°F are more preferred. However, like vapor pressure, an ECS compound's propensity to reduce flash point may be mitigated by appropriate means and is contemplated in this invention. Thus, the compound's causal increase in burning velocity and/or reduction of combustion temperature must be weighted against flash point temperature reductions or vapor pressure increases.

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ECS compounds, which are non-corrosive and/or which do not adversely effect seals or elastomers are preferred. However, corrosion inhibitors are contemplated, if necessary. For an example, a suitable inhibitor is "DC1 11" available from Du Pont. It is contemplated that this inhibitor should be used at the approximate concentrations of 20 to 30 ppm.

Preferred ECS compounds employed in liquid fuels should have low melting points, below 32°F and preferably below -0°F, or more preferably below -40°F or below -50°F, and most preferably below -80°F. Lower temperatures are also preferred. However, temperature reducing additives such as ethylene glycol monomethyl ether may be employed, if necessary. Again, the ECS compound's causal increase in burning velocity and/or reduction of combustion temperature must be weighted against less than desirable melting points.

It is preferred, though not required, that the ECS compound not be toxic, or at least not highly toxic, or associated with adverse toxicity. It is also preferred that the compound be pumpable at low temperatures, have suitable ignition quality, and be thermally stable as a fuel additive, although additives to correct poor thermal stability may be employed.

ECS compounds need not contain oxygen. However, ECS compounds containing oxygen are preferred. Those containing at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, or 50% or more oxygen by weight are desirable. Oxygen

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concentrations greater than 25% by weight are preferred. Most preferred are greater than 40% concentrations.

The amount of oxygen introduced into the system of critical import in advanced high velocity applications. It is contemplated that higher velocity, higher oxygen containing ECS compounds, particularly those with high latent heats of vaporization, represent the more preferred compounds in advanced applications.

10     Example 19

15     A method of creating a pre-combustion composition derived from a fuel exclusively containing one or more ECS compound(s) of high latent heat of evaporation, wherein said latent heat of vaporization exceeds 200 to 250 btu/lb @ 60°F, more preferably exceeding 300 btu/lb @ 60°F (or equivalent standard if not liquid); said method comprising vaporizing or injecting an atomized ECS compound having suitable average particle size (less than 70 microns, more preferably less than 60 micron) under suitable pressure into an air breathing combustion system, and introducing sufficient temperature to cause ignition; wherein upon either compression, pre-ignition, ignition, post ignition, pre-combustion and/or at combustion, the fuel's decomposition into high kinetic energy enhanced combustion vapor capable of rapidly diffusing in front of the flame is complete.

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Example 20

The method of example 19, wherein said enhanced combustion vapor is a post-ignition pre-combustion vapor of extremely high kinetic energy.

5

Example 21

The method of example 19-20, wherein said high kinetic vapor has a high latent heat of vaporization exceeding 26, preferably 29 to 34, or more,  $\text{kJ mol}^{-1}$  (measured at boiling temperature).

10

Example 22

The method of examples 19-21, wherein said combustion vapor has a laminar burning velocity exceeding 48 cm/sec (55, 60, 65, 70, 80 or more, measured at ambient conditions).

15

Example 23

The method of 19 wherein the pre-combustion vapor is a product derived from dimethyl carbonate.

20

Example 24

The method of 19-23, wherein a combustion improving amount of a high energy releasing metallic vapor having high heating value greater than 4,000 Kcal/kg, preferably greater than 5,000, 7,000, 8,000, 9,000, 9,800, 9,900, 10,000, 10,200, 10,400, 10,500, 10,600, 11,000, 11,500,

25

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Kcal/Kg, and more preferably greater than 12,000, 12,500, 13,000, 14,000, 15,000 Kcal/Kg or more, is additionally incorporated into said combustion vapor.

5     Example 25

          The method 19, 24, wherein said vapor additionally comprises a vapor derived from a carbonaceous co-fuel, such that said carbonaceous vapor on a mass basis is the majoritarian vapor; whereby combustion burning velocity of  
10     resultant vapor is increased by at least 5% and combustion temperatures are reduced by at least 10<sup>0</sup>F over vapor of the co-fuel only.

Example 26

15           The method of 25, wherein the co-fuel vapor is derived from an alternative fuel, hydrogen, petroleum gas, liquefied petroleum gas, LPG-propane, LPG-butane, natural gas, natural gas liquids, methane, ethane, propane, n-butane, propane-butane mixture, fuel methanol, e.g. M 80,  
20     M 90, or M 85 fuels, fuel ethanol, biomass fuels, vegetable oil fuels, automotive gasoline, aviation gasoline fuels, including grade 80, grade 100, grade 100ll, conventional automotive gasolines, reformulated gasolines, low vapor pressure gasolines, low sulfur gasolines, kerosine, wide  
25     range boiling fuels, gas turbine fuels, aviation jet turbine fuels including JP-4, JP-5, JP-7, JP-8, JP-9, JP-10, TS, Jet A-1, Jet A, Jet B, military aviation gasolines, missile fuels, solid and liquid rocket fuels,

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monopropellant, multipropellant fuels, hypergolic fuels, gas oil turbine-engine fuels, including grades 0-4, stratified-charged engine fuels, diesel fuels, including Grade low sulfur No. 1-D, Grade low sulfur No. 2-D, Grade No. 1-D, Grade No. 2-D, and Grade No 4-D, and older grades Type C-B, Type T-T, Type R-R, Type S-M, reformulated diesel fuels, fuel oils, including Grade 1, Grade 2, Grade 4 (light), Grade 4, Grade 5 (light), Grade 5 (heavy), Grade 6, heavy diesel fuels for marine or railroad, including those complying with ISO DIS 8217 and BS MA 100 standards, various distillate oils, residual type oils, cycle oils, light cycle oils, light cycle gas oils, heavy cycle oils, heating oils, heavy cycle gas oils, vacuum oils, burner oils, furnace oils, coal liquids, SRC-II middle distillate coal fuels, near coal liquids, powdered coal, tar sand fuels, shale oil fuels, hydrazine, ammonia acetylene, and fuels meeting ASTM specifications, EPA certification standards, industry and/or governmental specifications, present and future, including mixtures thereof.

#### Example 26a

The method of 19, 25, 26, wherein a co-fuel vapor is a substituent vapor of combustion; and wherein the combustion of said vapors power an engine under moderate or greater load conditions; whereby fuel economy and/or thermal efficiencies are increased over co-fuel operation alone by 0.5% to 20.0%, or more (2% to 30% preferred).

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Example 27

The method of 19, 25, 26, wherein said vapor additionally contains at least one vapor from an engine, carburetor and/or induction/injection system cleaning  
5 detergent/dispersant, including commercially available long-chain dibasic acid derivatives (e.g. succinimides such as HiTec 4450), long-chain aliphatic polyamines (e.g. polyisobutenyl polyamine), or long chain Mannich bases, and/or an ashless detergents, including a polyether amine,  
10 polyalkenyl amine, alkenyl succinimide, polyether amide amine, and mixture, and an antioxidant, demulsifer, emulsifer corrosion inhibitor, aromatic solvent, scavenger, diluent oil, mutual solvent, metal deactivator, and mixture.

15

Example 28

The method of example 19-27, wherein said vapor is combusted in an engine or combustor selected from group consisting of rocket engine, Brayton cycle engine, gas oil  
20 turbine, aviation jet turbine, diesel, marine, locomotive, aviation gas engine, automotive engine, oil burner, residue burner, oil furnace, gas burner, gas furnace, internal compression engine, spark-ignited internal combustion engine, lean burn, fast burn, external combustion Stirling  
25 or Rankine engine, Otto cycle engine, or catalyst system.



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METALS PRACTICE

Fuel chemistry, combustion factors, and operating system will determine most advantageous metallic concentrations. For example, high altitude pulse propulsion systems are likely, like rockets, to require significant concentrations. The preferred amount of metals contemplated by this invention requires that combustion be improved and/or pollutants reduced. Thus, depending upon combustion systems, combustion temperatures and combustion velocity, fuel injection factors, oxygen content, and the like, metallics and their respective concentrations can vary greatly.

In the practice of Applicant's invention the metallic is a propellant or co-propellant. Thus, the hydrogen content of the metallic should be maximized, to the extent possible. Metallic hydrides or similar compounds are desirable.

It is an express embodiment that the combustion of the metallic in Applicant's invention be by means of vapor phase burning, e.g. wherein the combustion process does not take place on the surface of the metal or on and within a molten layer of oxide covering the metal. Applicant's vapor phase burning is characterized by a high burning rate and the presence of a luminous reaction zone that extends some distance from the metal's surface, and the formation of oxide particles in the submicron range.

As a component of Applicant's invention, in order to achieve the above object, Applicant prefers the metal's

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oxide boiling point be greater than the boiling point of the metal. It is also preferred that the metal be introduced into the combustor as a vapor, however solid or particulate introduction is acceptable, so long as the above object is met. In solid fuel applications, it is contemplated the metallic may be introduced as a solid and in hybrid applications as either a solid or liquid.

It is preferred that the temperatures of combustion be greater than the metal's boiling temperature.

It has been found that higher weight oxygen concentrations in fuel compositions, particularly with Applicant's oxygenated combustion enhancing compounds, permit higher acceptable metallic concentrations. Generally, the higher the average fuel's density, the higher permissible metallic concentrations.

Applicant has found that higher Mn concentrations generally translate into higher heat releases. But that is not to say there are no upper limits. Combustion thermal dynamics will dictate upper limits.

Manganese concentrations will vary substantially, and may vary from 0.001 to over 7.50 grams Mn/gal, 0.001 to over 10.00 grams Mn/gal, 0.001 to over 15.00 grams Mn/gal, 0.001 to over 20.0 grams Mn/gal., 0.001 to over 30.00 grams/Mn/gal., 0.001 to over 50.00 grams/Mn/gal. or more. In certain applications, concentrations greater than 1/32, 1/16, 1/4, 1/2, 3/4, 1, 1.5, 2.0, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 5.0, 7.5, 10, 15, 20, 25, 26, 27, 30, 33, 35, or 40 grams may be desirable. In rocket propellants, metallic/Mn

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concentrations can be on the order of 100, 200, 200 to 500, 600, 800 to 1000.0 grams/gal, especially in hypergolic conditions.

5        However, manganese ranges for most traditional applications will be about 0.001 to about 5.00 grams Mn/gal, 0.001 to about 3.00 grams Mn/gal, 0.001 to about 2.00 grams Mn/gal, 0.001 to 1.00 grams Mn/gal, 0.001 to about 0.50 grams Mn/gal, 0.001 to 0.375 grams Mn/gal, 0.001 to about 0.25 grams Mn/gal, or even 0.001 to 0.125 grams  
10       Mn/gal, or even 0.001 to 0.0625 grams Mn/gal of composition.

      In the case of gasolines manganese concentrations greater than 1/32, 1/16 gram manganese per gallon are expressly contemplated and desireable. In the case of  
15       diesel fuel applications manganese concentrations greater than 1.0% by weight of the fuel or approximately 25 to 33 grams/gal. are contemplated.

      Ranges will also vary depending upon the fuels weight, regulations, advance applications, and the extent  
20       combustion systems are modified to take advantage of the high energy nature of Applicant's invention. The ranges of other metallics contemplated in this invention will enjoy ranges similar to manganese's, but vary on a metallic by metallic basis.

25       In accordance with this invention, Applicant's fuels will contain that amount of Mn and/or other non-lead metallic, which constitutes a combustion improving amount consistent with the fuel composition, its combustion

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system, the efficiencies desired, legal and/or environmental considerations.

However, it is expressly contemplated that in certain application's of Applicant's invention, Applicant's fuel  
5 will be absent any metallic, e.g. be metal free. That is, Applicant's invention, by accelerating burning velocity and/or reducing combustion temperatures, can be employed in non-metallic fuels, but which due to their combustion chemistry, and/or operating conditions, require hazardous  
10 combustion emission reductions and/or fuel economy improvements. Such fuels are improved by Applicant's invention.

It is an embodiment of this invention to substitute or combine various metallics (e.g. mix them), including  
15 substituting or mixing different metallics of different groups or with the same group, or substituting or mixing metals of the same group or subgroup, with each other or any other group or metal. Applicant contemplates great variability and wide latitude of substitution and/or  
20 mixing, including mix ratios, mix ingredients, etc. See for example U.S. Patents 3,353,938; 3,718,444; 4,139,349.

Thus, it is expressly contemplated that non-lead organo-metallics, non-lead inorganic metallics, and/or their related high heat releasing compounds, may be mixed  
25 in varying proportions, and/or substituted for each other and/or replaced by any non-lead metallic or non-metallic (organic or inorganic) accomplishing the object of this invention.

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It is contemplated that Applicant's metals may be blended with one or more of metals or non-metals in varying proportions to achieve synergistic improvements in heat releases, burning velocity, thermal efficiency, emissions, power generation, and the like.

Contemplated metallics include all non-lead metals and related compounds whose combustion product has negative high heat of formation. Contemplated metals should have high heats of combustion or heating values, preferably in excess of 3,000, 4,000, 5,000, or 6,000 Kcal/kg. Values in excess of 9,000 to 10,000 Kcal/Kg are preferred. More preferred are those in excess of 11,000 to 13,000, 14,000, or higher, Kcal/Kg.

Preferred negative heats of formation, for example of related metallic oxides, should exceed -150,000 gr calories/mole. More preferred are -200,000, -225,000, -275,000, -300,000, -350,000, - 400,000 gr calories/mole., and greater.

It desirable that the elemental metal be of a lower molecular weight, if practical. Non-limiting examples of acceptable metals include aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium, gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybdenum, nickel, niobium, phosphorus, potassium, pallium, rubibidium, sodium, tin, zinc, praseodymium, rhenium, salane, vanadium. Applicant's metals may be organo-metallics or inorganic.

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Transition metals and metals found in 1A, 1B, 2A, 2B, 3B of the periodic table of elements and their cyclomatic compounds, including cyclopentadienyl carbonyls are expressly desirable. Their preparation is set forth in  
5 U.S. Patents Nos. 2,818,416, 3,127,351, 2,818,417, 2,839,552 (incorporated by reference). Applicant has found that methyl cyclopentadienyl tricarbonyl groups to be effective.

Cyclomatic compounds that include metals found in 4B,  
10 5B, 6B, 7B, group 8 are also contemplated. Cyclomatic compounds containing more than one metals are contemplated.

Metals and their compounds found in 3A of the Periodic Table of Elements, particularly boron and aluminum are expressly contemplated. Metals may be introduced into  
15 combustion with the ECS compound, or in a number of other ways, including via soluble compounds, mutual dispersants/solvents, colloidal media, suspension media, separate injection.

Applicant believes that those metallics which are  
20 generally fuel soluble, having melting and boiling ranges compatible with liquid hydrocarbon combustion present the best immediate option.

Because Applicant's invention also contemplates gaseous and solid ECS compounds and gaseous and solid co-  
25 fuels, metals and/or their related compounds that are gaseous and/or solid are also contemplated.

Applicant generally prefers elemental metals of low molecular weight and their compounds, although their

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heating value and the nature of any co-fuel and combustion system will also dictate choice. It is also preferred the combustion products of element and/or its compounds be environmentally friendly, e.g. low toxicity.

5           Applicant recognizes that there is a wide number of  
metallics available in the practice of instant invention. A limited number of examples include cyclopentadienyl  
methylcyclopentadienyl iron, ferrocene, methylferrocene,  
and butadiene iron tricarbonyl, butadiene iron tricarbonyl,  
10       dicyclopentadienyl iron and dicyclopentadienyl iron  
compounds (see U.S. Patents 2,680,; 2,804,468; 3,341,311);  
nickel, cyclopentadienyl nickel nitrosyl; molybdenum  
hexacarbonyl, cyclopentadienyl molybdenum carbonyls (see  
U.S. Patent 3,272,606, 3,718,444), compounds of technetium,  
15       magnesium, rhenium (see Canadian Patent #1073207.),  
diborane, tetraborane, hexaborane, and mixture. It is  
contemplated that organo and non-organic species of these  
metals will be employed. U.S. Patent # 2,818,416 sets forth  
many       such       trimethylaluminum,       triethylaluminum,  
20       dimethylberyllium, boron hydrate, boron hydride, boron  
anhydride, triethylboron (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>B; compounds of boron with  
hydrogen and lithium, pentaborane, decaborane, barazole,  
aluminum borohydride, beryllium borohydride, lithium  
borohydride, and mixtures thereof; light metals compounds  
25       (CH<sub>3</sub>)<sub>3</sub>NBH(CH<sub>3</sub>)<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>BI, Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, C<sub>4</sub>H<sub>9</sub>B(OH)<sub>2</sub>, Al(BH<sub>4</sub>)<sub>2</sub>,  
Be(BH<sub>4</sub>)<sub>2</sub>, LiBH<sub>4</sub>, B(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, (BO)<sub>3</sub>(OCH<sub>3</sub>)<sub>3</sub>; Zn(CH<sub>3</sub>)<sub>2</sub>.  
Compounds with multiple metals are expressly contemplated.

A preferred cyclomatic manganese tricarbonyl is

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cyclopentadienyl manganese tricarbonyl. A more preferred cyclomatic manganese tricarbonyl is methyl cyclopentadienyl manganese (MMT).

Non-limiting examples of acceptable substitutes include the alkenyl, aralkyl, aralkenyl, cycloalkyl, cycloalkenyl, aryl and alkenyl groups. Illustrative and other non-limiting examples of acceptable cyclomatic manganese tricarbonyl antiknock compounds include benzylenecyclopentadienyl manganese tricarbonyl; 1,2-dipropyl 3-cyclohexylcyclopentadienyl manganese tricarbonyl; 1,2-diphenylcyclopentadienyl manganese tricarbonyl; 3-propenylidenyl manganese tricarbonyl; 2-tolylindenyl manganese tricarbonyl; fluorenyl manganese tricarbonyl; 2,3,4,7 - propylfluorenyl manganese tricarbonyl; 3-naphthylfluorenyl manganese tricarbonyl; 4,5,6,7-tetrahydroindenyl manganese tricarbonyl; 3-ethenyl-4,7-dihydroindenyl manganese tricarbonyl; 2-ethyl 3 (α-phenylethenyl) 4,5,6,7 tetrahydroindenyl manganese tricarbonyl; 3 - (α-cyclohexylidenethenyl) -4,7 - dihydroindenyl manganese tricarbonyl; 1,2,3,4,5,6,7,8 - octahydrofluorenyl manganese tricarbonyl and the like. Mixtures of such compounds can also be used. The above compounds can be generally prepared by methods that are known in the art.

In the practice of Applicant's invention the heavy high melting point metal oxides of manganese (Mn<sub>3</sub>O<sub>4</sub>), Aluminum (Al<sub>2</sub>O<sub>3</sub>), cobalt, copper, gallium, lithium, magnesium, nickel, niobium, tin, zinc, vanadium, et al, are



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no longer problematic. Thus, high energy releasing metallic compounds can unexpectedly be employed in the instant invention.

Thus, those metallics having very high heating values in combustion, if not for the formation of high melting temperature oxides on engine and other surfaces and/or due the hazardous combustion produce generated, can now be unexpectedly employed. Furthermore, they can be employed in concentrations not hereto for thought practical/acceptable (e.g. Mn above 1/32 gr/gal in gasolines).

Applicant has found magnesium and its related combustion compounds to be a particularly effective metallic, and is thus desireable. Promoters such as Li and LH are contemplated if circumstances require.

All such metallics, which advance the object of this invention and/or benefited from the practice of this invention, are a specific embodiment and contemplated in the claims hereto.

Other non-limiting examples of non-lead metallics have been set forth in the specification. Many additional contemplated metallics are known in the art. Applicant anticipates the development of designer metals as a result of this invention, and contemplates their usage as well.

#### ECS COMPOUND SUBSTITUTION

Applicant's teachings herein referring to any specific ECS compound, for example, dimethyl carbonate, may be substituted for any other ECS compound or component, which

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accomplishes Applicant's object and is consistent with the requirements of the fuel, combustion and/or emissions systems, etc. Thus, it is contemplated oft substitutions of compounds disclosed herein for any ECS compound may be made, so long as the object of Applicant's invention is maintained. However, Applicant is mindful that all ECS compounds are not equal, and may not have the efficacy of the original or substituted compound. Thus, substitution can not be made without appropriate consideration.

10 In other words, it is the express embodiment of this invention to substitute, combine, mix dimethyl carbonate with hydrogen, carbon monoxide, methanol, methylal, ethanol, n-propanol, i-propanol, methylene di methyl ether, dimethyl carbonate, methyl tertiary butyl ether (MTBE),  
15 ethyl tertiary butyl ether (ETBE), methyl tertiary amyl ether, diisopropyl ether, C<sub>3</sub> to C<sub>6</sub> lower molecular weight alcohols, dimethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, water, hydrogen peroxide and any other ECS compound, or mixture.

20 Additional non-limiting possible substitutions for dimethyl carbonate include ECS compounds selected from C2-C12 aldehydes, C2-C12 ethers (MTBE, ETBE, 2,2-diethyl-1,3-propanediol), C4 - C15 alcohols (furon, furfuryl, 1-hexanol, 2-hexanol, 3-hexanol, and polyethoxyethanols), C2-  
25 C12 oxides (2-methylfuran, methyltetrahydrofuran), C3 - C15 ketones (acetone, 2,3 butanedione, 2,5 hexanodione, 2,4 pentanedione, cyclopentanone), C3 -C15 esters (isopropyl acetate, ethyl acrylate), C3 - C12 diesters, C5 - C12

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phenols (P-cresal, 2, 4 xylenal, 3-methoxyphenal), C5-C20 glycol ethers (including diethylene dimethyl ether, diethylene diethyl ether, diethylene dipropyl ether, diethylene dibutyl ether, including diethylene monomethyl ether, diethylene monoethyl ether, diethylene monobutyl ether), C4-C20 carbonates having boiling temperatures above 90°F or more preferably 120°F, C5-C25 dicarbonates having boiling temperatures above 90°F or more preferably 120°F, organic and inorganic peroxides, including di-tertiary butyl peroxide, alkyl peroxides, alkyl hydroperoxides, 2.5 dimethyl 2.5 di(tertiary butyl peroxy) hexane, tertiary butylcumyl peroxide, di(tertiaryamyl) peroxide, tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, alkyl nitrate additives, including ethyl-hexyl nitrate and isopropyl nitrate, and mixtures thereof. Heavier ECS compounds may be used in lieu of the preferred dimethyl carbonate or oxygenated/ECS means and/or may be used in addition, with or without solvents.

The substituted ethers contemplated in this invention include branched and straight chain ethers, di ethers having two oxygen and dual ether linkage, and tri ethers having three oxygens and multiple ether linkages. Non-limiting examples include dimethyl ether, methyl ethyl ether, di ethyl ether, ethyl propyl ether, methyl normal propyl ether, ethyl isopropyl ether, methyl isopropyl ether, ethyl normal propyl ether, propyl ether, propyl isopropyl ether, diisopropyl ether, ethyl tertiary butyl ether, ethyl secondary butyl ether, methyl normal butyl

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ether, methyl isobutyl ether, methyl tertiary butyl ether, methyl secondary butyl ether, methyl normal amyl ether, methyl secondary amyl ether, methyl tertiary amyl ether, and methyl iso amyl ether. Additional non-limiting  
5 examples of acceptable di ethers (having two oxygens and dual ether linkage) include methylene di methyl ether, methylene di ethyl ether, methylene di propyl ether, methylene di butyl ether, and methylene di isopropyl ether.

In the practice of this invention, substituted higher  
10 molecular weight C4 ethers are particularly desirable, especially when employed in diesel fuel, fuel oil, and/or turbine fuels. The production of ethers is also well known to the art. See for example, U.S. Patents 4,262,145; 4,175,210; 4,252,541; 4,270,929; 3,482,952; 2,384,866;  
15 1,488,605; 4,256,465; 4,267,393; 4,330,679; 4,299,999; 4,302,298; 4,310,710; 4,324,924; 4,329,516; 4,336,407; 4,320,233; 2,874,033; 3,912,463; 4,297,172; 4,334,890, et al.

Substituted ECS ketones may include lower alkenyl  
20 ketones. Representative lower alkenyl ketones would include diethyl ketone, methyl ethyl ketone, cyclohexanone, cyclopentanone, methyl isobutyl ketone, ethyl butyl ketone, butyl isobutyl ketone, ethyl propyl ketone, and the like. Other ketones include acetone, diacetone alcohol,  
25 diisobutyl ketone, isophorone, methyl amyl ketone, methyl isoamyl ketone, methyl propyl ketone, and the like. A representative cyclic ketone would be ethyl phenyl ketone.

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Substituted ECS esters include anisole (methyl ester of benzene), isopropyl acetate, and ethyl acrylate.

Substituted ECS carbonates, which are particularly preferred include symmetrical dialkyl carbonates in which the alkyl groups are derived from lower unbranched primary alcohols such as methanol and ethanol, for example, dimethyl carbonate and diethyl carbonate. Higher symmetrical dialkyl carbonates such as di-n-butyl carbonate, di-t-butyl carbonate, dipropyl carbonate, and dicarbonates such as dimethyl dicarbonate and diethyl carbonate, alkyl phenyl carbonates such as t-butyl phenyl carbonate, and cyclic alkylene carbonates such as propylene carbonate, ethylene carbonate, and butylene carbonate, as well as other organic carbonates such as isopropyl cyclohexyl carbonate, methyl n-butyl carbonate, isobutylene carbonate and diisopropyl carbonate, are also preferred. Unsymmetrical dialkyl carbonates may also be employed, including methyl t-butyl carbonate, ethyl t-butyl carbonate, methyl t-amyl carbonate, ethyl t-amyl carbonate. Mixtures of carbonates are also contemplated.

Thus, for purposes of achieving the object of increasing burning velocity and reducing combustion temperatures, etc., in the disclosure of this invention setting forth dimethyl carbonate (DMC), disclosure may be read to contain a substituted ECS compound and/or alternatively be read to additionally include and/or contain other members, analogues or homologues of any ECS compound and/or of the family of ECS compounds and mixture,

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including those of higher molecular weight (or higher boiling temperature), so long as they are capable of increasing burning velocity and/or reducing combustion temperatures.

5           It is also contemplated that ECS compounds may be substituted for each other or for non-ECS compounds, or not employed at all, so long as the object of increasing burning velocity and/or reducing combustion temperatures occur by other suitable means.

10           ECS compounds may be blended with one or more of themselves in varying proportions to achieve synergistic improvements in burning velocity and temperature reductions.

          In circumstances where ECS compound usage raises  
15       concerns of flash point, volatility, vapor pressure, corrosivity, elastomer swelling, solubility, hydrolysis, and the like, co-solvent practice employing higher molecular weight alcohols, ethers, ketones, carbonates, etc., may be desirable. See my EPO Patent # 0235280 for  
20       discussion on co-solvent practice.

          Additionally, Applicant notes his preferred  $\text{OCH}_3$  (methoxy radical) combustion enhancement structure is structure common to methanol, methylene di methyl ether (methylal, MDME), and carbonic acid dimethyl ester  
25       (dimethyl carbonate), MTBE, and the like. Applicant's preferred OH combustion enhancement structure is common to his alcohols, most notably methanol.

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Applicant also recognizes that certain duplication exists between various classes in this invention. For example, ECS chemistry may contain certain metals, certain metals may be propellant fuels, ect. It is contemplated  
5 that certain compounds will have multiple utility.

#### MECHANICAL MEANS

It is contemplated that multiple mechanical means will be employed to enhance burning velocity and/or reduce  
10 combustion temperatures. Such mechanical means may be independent of a ECS or chemical means, or may be in concert therewith. For example, ECS compounds which have limited burning velocities and/or reduced latent heats of vaporization may be enhanced by mechanical means, e.g.  
15 small particle atomization, cooling systems, turbulent compression chambers, turbo-charging, etc.

Thus, it is anticipated that the mechanical means of Applicant's invention will vary depending upon the fuel and the combustion system contemplated. For example, neat ECS  
20 fuel applications, having higher burning velocities, will incorporate differing mechanical means, than for example, a ECS fuel and base fuel combination, having a lower burning velocity used in a low compression ratio combustion system.

25 The mechanical means of this invention include: fuel injection systems, especially those capable of directing a fine uniform atomized spray of vapors at enhanced dynamic flow rates and pressures at desirable angles into



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combustion chambers (combustors, burners, etc.) advanced evaporators, combustor designs enhancing combustion turbulence, higher combustion chamber inlet pressures (e.g. higher compression ratios), swirl combustors, spherical combustors, divided chambers, combustors enhancing combustion efficiency, combustor design enhancing fuel-air mixing, combustion chamber (combustor) design enhancing turbulence and/or fuel-air mixing, engine design maximizing compression (inlet pressure) advantages, engine design maximizing increased power combustion pressure (pressure densities), engine design maximizing lower combustion temperatures, and/or the other advantages of Applicant's invention.

Additional mechanical means, which may be employed and/or adapted, include lean burn systems, catalytic combustors/combustion systems, pre-mixed combustor, diffusion flame combustors, lean premixed pre-evaporizing combustor, pre-evaporizing premixing combustor, variable compression ratio engines, direct injection stratified charge engines, turbo-chargers, after-cooling systems, re-entrant combustion chambers, pre-combustion chambers, re-matched inlet port swirl systems, reduced quenching systems, reduced heat transfer systems, enhanced fuel-air mixing systems, enhanced spray atomizer kinetic energy systems, injector designs enhancing fuel-air mixing, water injection systems, and the like.

In the practice of this invention lean-burn and/or fast burn combustion systems are desirable for purposes of



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enhancing Applicant's object, particularly with advanced higher oxygen containing fuels.

5 Mechanical systems employing combustion chambers/combustors, which enhance turbulence are preferred. Non-limiting examples include tumble air motion systems, four valve pent roof combustion chambers, swirl combustion chambers, indirect injection combustion chambers, indirect injection swirl combustion chambers, direct injection combustion chambers, and combustion  
10 chambers where geometry, hole diameter, spray angle, compression ratio, and the like, act to enhance turbulence are preferred.

Injection timing, fuel metering, injection pressures, injection pressure drop, nozzle design, inlet air  
15 temperatures, inlet air pressure, droplet size, velocity, pressure and temperature of injected droplets, and combustion chamber geometry are among the influential factors in maximizing the benefits of Applicant's invention, and are incorporated as an express embodiment of  
20 this invention.

For example, by varying the nozzle angle, nozzle throat angle, nozzle jet spray centerline eccentricity, spray radius (sphere radius) in a pre-combustion (swirl chamber), and by modifying injection timing, rate,  
25 duration, and the like, Applicant can maximize the beneficial attributes of his invention. It is noted, gasoline, diesel fuel, jet turbine, gas oil turbine, fuel oil burner applications are expressly contemplated.

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Thus, application, including the injection of highly atomized vapors into the combustion chamber/combustor, and the like, is a particularly desirable object of this invention, especially in turbine, diesel, and fuel oils.

5       Applicant contemplates a multiplicity of injection and atomization means. Differing fuels, fuel systems, combustion stems require differing injection, atomizing systems, pressures, temperatures, and the like. Obviously, gasoline systems are different than, for example, Grade No.  
10   4-6 fuel oils, which in the practice of this invention, require devices to atomize higher viscosities, and to inject them into burner or combustion chambers at greater pressures. The gasoline systems of Applicant invention contemplate injection manifold systems, whereas the diesel  
15   systems contemplate direct/indirect injection cylinder systems, etc.

With Applicant's high latent heat of vaporization fuels, a vacuum effect occurs when introducing the charge into a cylinder. Consequently, varying fuel injection  
20   pressures, including low and very low pressures are contemplated.

Heavy diesel fuel, fuel oil, and related combustion systems require higher amounts of pressure, load sensing capability, and improved atomization features, when  
25   compared to gasoline systems. Jet aviation fuels have similar, yet differing requirements and must, for example, consider fuel flow ranges of 50:1.

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For example, in the practice of this invention, contemplated optimum gasoline fuel injection pressures are on the order of 1 to 5, 3 to 15, 5 to 20, 10 to 30, 15 to 45 psi. Optimal diesel fuel injection pressures are on the order of 1500 psi to 30,000 psi. Lower pressures injection, due to the vacuum effect of injecting certain ECS fuels, are expressly contemplated.

Examples of Applicant's non-limiting atomization systems include: single fluid and multifluid and/or fluid/gas atomizer jets, twin-fluid atomization, internal-mixing atomizers, pressure atomizer, Y-jet atomizers, spinning disk systems, air sprays systems, spray atomizers, vaporizing systems, airblast atomizers, including plain-jet, prefilming, flat air blast atomizer, centrifugal injectors, rotary atomization, rotary wheel injection, ultrasonic, acoustic atomizers and other existing and/or future systems. Air blast atomizers are desirable in the preferred practice of this invention.

Collaterally or alternatively to fuel injection systems, the use of vaporizing elements, including T-shape, L-shape and the like, are contemplated. Vaporizer elements are normally affixed to the flame tube, whereas fuel injectors are fixed in the combustor casing with the injector head being positioned inside the vaporizer tube.

In the practice of this invention, it is a principle object that the average particle size distribution of Applicant's fuel vapor, emitted from the atomization system (or evaporation system) into the combustor/ect., be of a

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size maximizing combustion attributes of this invention, and that its distribution in the combustion chamber be such to maximize burning velocity, latent heat of vaporization attributes, combustion pressure increases, etc.

5           Thus, it is a desired and an express embodiment of this invention that the particle (drop size) of injected or vaporized fuels in the combustion chamber be 1 to 70 microns. Preferable average particle sizes are 40 to 60 microns or less, more preferably from 30 to 50 microns, 20  
10   to 40 microns, 5 to 30 microns, or less, including 1 micron or submicron. There is no limitation to the reduction of vapor particle size so long as fuel vapor distribution characteristics are not adversely effected. Average  
15   particle sizes greater than 30, 40, 50, or 70 microns are acceptable if rapid diffusion of the vapor fraction occurs by other means, e.g. chemical means, and/or if smaller  
20   particle sizes hinder proper fuel distribution characteristic. However, believes that certain applications will require a minimum particle size of not greater than 5, 10, 20, 30, 40, 50, or 60 microns.

          It is also preferred that such injection systems maximize air-fuel mixing, to the maximum extent possible to enhance combustion. However, Applicant does not desire to employ too high a mixing rates so as to cause a high lean  
25   blow out limits or the like.

          In jet aviation applications, especially in high mach circumstances (where natural convection and diffusion is reduced), differing pressures from distinct fuel injection

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streams may be desirable. Additionally, fuel injection systems incorporating interacting parallel and transverse fuel injectors has been found to be useful in high mach circumstances. Mixing enhancement through combined parallel and transverse injection has also been found to be particularly effective and is expressly contemplated in this invention.

Injection pressure will vary substantially, with the higher pressures will be typically employed in heavier diesel and fuel oil applications of higher viscosity fuels. However, high pressure injection in gas turbines is more difficult due to the high fuel pressures necessary and the problems of controlling fuel distribution in the combustor. Thus, lower injection pressures are contemplated in many applications.

Thus, advanced fuel injection systems, which optimize the combustion and cooling characteristics of a fuel composition, so as to improve burning velocity are an essential and express embodiment of this invention.

In the practice of heavy diesel fuels and companion engines, higher injection pressures with retarded timing under full load conditions yields maximum mixing energy and enhances the burning velocity object of Applicant's invention and is thus preferred.

It has been found that lower injection pressures for heavier diesels fuel applications under high speed, but light load conditions, tends to minimize over-mixing and

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reduces hydrocarbon emissions and is also a preferred practice.

Simultaneous fuel injection, by adequate means employing one or more injection systems (e.g. a dual fuel injector), of similar or dissimilar physical state fuels, e.g. gas with a liquid, solid with a liquid, etc., is within the scope of this invention and expressly contemplated. Such application is expressly contemplated where the mixing of an ECS compound with a base co-fuel that may not be possible prior to fuel injection and/or to optimize combustion, which best occurs via separate injection. Separate injection is also contemplated when fuel mixing can not be achieved by other means prior to fuel injection and/or combustion.

For example, the introduction of a liquid hydrocarbon co-fuel and a gaseous ECS fuel, such as hydrogen into a combustion chamber or combustor would be accomplished by separate injection, tailored to the specific characteristics of the fuel, and combustion system, designed to maximize combustion burning velocity.

Thus, it is contemplated that dissimilar state fuel ingredients may be injected into a combustion system, simultaneously, by singular and/or separate means.

Various mixing and injection combinations of Applicant's ECS fuels, co-fuels, are contemplated in the context of advanced fuel injection systems and methodology.

In the case of jet aviation turbine applications, rate tailoring for fuel flow adjustments at altitude is

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especially preferred, as variations in combustion efficiency occur due to lower ambient pressures.

Improved pump line nozzle injection systems, unit injector systems, and/or other systems with high pressure capability, injection rate control, timing control, and/or other sensing controls are especially desirable. Injection systems which can control injection pressure, timing, rate metering, and/or combustion pressures are expressly contemplated.

In the practice of this invention, direct and indirect fuel injection systems are acceptable. However, direct injection systems are more desirable, especially for diesel applications. Direct fuel injection systems are also more desirable in view of maximizing the higher burning velocities of Applicant's ECS fuels.

A further embodiment, as noted above, is turbocharging and supercharging, which is highly preferred practice of this invention, especially in gasoline and diesel applications. Advanced air breathing, air pressure apparatus, and/or turbocharge systems, increasing intake air pressures, operate in conjunction ERG systems, are particularly desirable, and substantially enhance the object of this invention.

Advanced cooling, after cooling, and/or coolant systems may also be employed. For example, combustion temperatures can be reduced by reductions in engine coolant temperatures, inlet air temperatures reductions, and/or



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intake manifold heat inputs. All such means are within the scope of this invention.

Example 29

5           In combination, a combustion improving fuel containing a high latent heat of vaporization oxygenated based ECS compound and a combustion improving amount of a metallic, a combustion system, and an exhaust gas recirculation (ERG) system, wherein said fuel is combusted and exhaust gases  
10           are recirculated back into the combustion system.

Example 30

          The examples of 29, wherein the ERG system is a closed loop system.

15

Example 31

          The examples of 29-30, wherein the fuel is unleaded, the combustion system is for U.S. regulated gasolines, the combination additionally includes a regulated emission  
20           control system.

Example 32

          The example of 29, wherein the fuel contains oxygen in a concentration of 2.0% by wt. and a combustion improving  
25           amount of a cyclomatic manganese tricarbonyl compound in a concentration of 1/32 gram of mn.



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Example 33

The example of 32, wherein the fuel enjoys an increased burning velocity, and thermal efficiency of the system is improved; whereby fuel economy is increased by at least 0.5%, 1.0%, 2.0%, 5.0%, 10% or more.

Applicant's invention also contemplates use of exhaust after treatment systems, with non-limiting examples including ceramic liners, filters, traps, trap-oxidizers, and catalysts. The practice of employing emission exhaust catalyst, especially in automotive application is well known in the art.

In the practice of this invention it is contemplated, especially in automotive applications to employ an exhaust emissions catalyst (three way catalysts, preferably monolithic catalysts) and to simultaneously employ an on board oxygen sensor, which in part measures the efficiency of the catalyst.

In sum, it is the combination of Applicant's advance combustion improving fuels with applicant's mechanical and related systems, which together, represent significant departure from art.

Thus, it is an embodiment of this invention to vary and/or adapt the above mechanical means to achieve the highest utility of this invention.

**FUELS AND COMBUSTION SYSTEMS GENERALLY**

The combustors contemplated in the practice of this invention include geometric combustors (tubular, annular,

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tubo-annular, spherical), aerodynamic combustors (diffusion flame, premixing, staged, catalytic, and application combustors (aircraft, industrial, vehicular).

5 It is preferred in the practice of this invention to employ a diffusion flame combustor, wherein Applicant's combustion flames are further propagated by gaseous jet diffusion, advanced droplet evaporation, accelerated burning, and/or spray diffusion.

10 Thus, it is an embodiment to employ a diffusion flame combustor in combination with ECS fuels; whereby combustion emissions are improved, combustion is accelerated and/or there is a reduction of combustion temperatures.

15 Applicant's invention is particularly applicable in turbine applications, especially in aviation gas turbines, industrial gas turbines, marine gas turbines, and the like.

The physical state of fuels employed in this invention include a wide and narrow boiling range of liquid, semi-liquid, near-liquid, semi-solid, solid, and gaseous fuels, and mixture.

20 Applicant's neat fuel embodiment (e.g. ECS compound and metallic) has exceptional propulsion and environmental attributes, which are not limiting to internal combustion engines, aviation jet turbines, gas oil turbines, furnaces, burners, air breathing propulsion systems, or rocket  
25 engines.

Applicant's neat fuel is a stand alone fuel, which may be used potentially in any combustion system. Albeit, modification of existing combustors may be required to

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accommodate the combustion maximizing and thermal dynamic aspects of such neat applications.

It is also an embodiment of this invention to incorporate advanced combustion systems, capable of better  
5 converting higher amounts of free energy under higher pressures and/or improved thermal efficiencies resulting from the usage of Applicant's fuels. It is anticipated, system modifications and new design will be made to maximize the advantage of the neat, near neat, majority  
10 neat, or minority neat ECS fuels of Applicant's invention.

Hence, it is an embodiment of this invention to incorporate such advanced combustion systems with Applicant's fuels.

It is also an express embodiment of Applicant's  
15 invention to employ an ECS compound, or mixture, solely by itself, with or without a combustion improving amount of non-lead metallic. However, it is a preferred embodiment to employ an ECS compound, or mixture, together with at least one non-leaded metallic ("ECS Fuel"). It is also an  
20 embodiment that Applicant's ECS fuel may contain at least one additional oxidizer and/or at least one addition propellant or a co-fuel.

In co-fuel practice, e.g. where ECS fuel is combined with hydrogen and/or a carbonaceous fuel, RVP reduction is  
25 an express embodiment. However, finished fuels contemplated include those whose RVP ranges from 0.01 psi to 1000.0 psi, 2.0 psi to 200.0 psi, 2.0 psi to 40.0 psi, 1.0 psi to 20.0 psi, 1.0 to 10.0, 1.0 to 8.0 psi, 1.0 psi to 7.5 psi, 1.0

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to 7.0 psi, 1.0 to 6.5 psi, 1.0 to 6.0 psi, 1.0 to 3.0 psi, 1.0 to 2.0 psi, or lower.

It is also an express embodiment to optimize flash point in fuels that specify certain flash point temperatures. It is anticipated that co-solvent practice, tailoring of hydrocarbon fractions (so as to increase flash point), salts, soaps, and other additives will be employed as required to reduce RVP and/or increase flash point. Such practice is contemplated.

#### Example 34

A composition comprising an ECS compound and a combustion improving amount of at least one non-lead metallic.

#### Example 35

The composition of 34, additionally containing an oxidant and/or co-fuel.

Thus, Applicant's invention embodies a neat, essentially neat, majority neat ECS fuel, including compositions containing greater than 50% ECS compound(s) by volume. It also embodies a substantial majority, a minority, or substantial minority application, e.g. greater than 0.5%, 1.0%, 1.5%, 1.8%, 2.0%, 2.7%, 3.0%, 3.5%, 3.7%, 4.0%, 5%, 10%, 15%, 20%, 25%, 30%, 40% by volume, or weight) of an ECS fuel, normally with a co-fuel ("Base Fuel or Co-Fuel").

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In the practice of Applicant's invention, the most preferred neat ECS fuels containing Mn include dimethyl carbonate, methanol, hydrogen, methylal, methane hydrate, hydrazine, and mixtures thereof.

5           It is initially contemplated Applicant's ECS fuels will likely be incorporated in minority volumes into co-fuels concurrently in the market.

          However, with greater concentrations of ECS fuels as a volume percent of the finished fuel, combustion and  
10       emission properties increase dramatically.

          In the more specific co-fuel applications below, Applicant intends that his disclosure of one co-fuel be appropriately applied to any other co-fuel, where application is appropriate (e.g. anti-oxidants or  
15       detergents of one co-fuel class can be used with other co-fuel classes, etc.).

#### **JET AVIATION TURBINE FUELS AND RELATED TURBINE SYSTEMS**

          This invention expressly contemplates jet aviation  
20       turbine fuel application and co-fuel application. Applicant anticipates wide application in a wide range of jet fuels, aviation turbine engine fuels, including fuels for propulsion and lift engines, starters and auxiliary units.

          The practice of this invention expressly embodies  
25       aviation turbine, resultant aviation turbine fuels (ECS fuel and co-fuel) or co-fuels, which meet ASTM D 1655 standards, including Jet A, Jet A-1 (a relatively high flash point distillate of the kerosine type), and Jet B-A

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(a relatively wide boiling range volatile distillate). Other jet turbine grades are contemplated, including those meeting IATA guidance manual specifications and military aviation turbine specifications, such as MIL-T-5624, MIL-T-83133, and MIL-P-87107. Thus, Applicant incorporates by reference the numerous specifications of aviation and gas turbine fuel's in Chapter 2, "Gas Turbine Fuels," L. Gardner and R.B. Whyte, Design of Modern Turbine Combustors, Academic Press, 1990 (pages 81-227).

The aviation turbine fuels of this invention, except as otherwise specified herein, consist of blends of refined hydrocarbons derived from crude petroleum, natural gasoline, or blends thereof with synthetic hydrocarbons. They are generally a mixture of hydrocarbons (i.e. paraffins, cycloparaffins, aromatics, and olefins, plus trace levels of heteroatoms such as sulfur compounds) and blended from straight run distillate fractions, which have been subjected to some form of additional processing.

Aviation turbine fuels, consisting of minor and major portions of ECS material, as disclosed herein are specifically contemplated.

Applicant's invention expressly contemplates gas turbines and air-breathing propulsion systems. Such non-limiting systems include turbojet, turboprop, ducted fan, ram jet, scram jets, ducted jet, pulse jet systems, and their many variations. These systems are contemplated in the instant practice of aviation turbine fuels.

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For example, non-limiting gas turbine configurations include basic, one intercooling, two intercooling, isothermal intercooling, one reheating, two reheating, isothermal reheating, one intercooling and one reheating, two intercooling and two reheating, isothermal intercooling and isothermal reheating, regeneration, regeneration with basic gas turbine, regeneration with one intercooling, regeneration with one reheating, regeneration with one intercooling and one interheating, regeneration with two intercooling and two reheating, and regeneration with isothermal intercooling and isothermal reheating.

Non-limiting examples of "turbo jet" air breathing propulsion systems include: basic, intercooling, reheating, intercooling and reheating, after-burning, intercooling and reheating. Non-limiting examples of "turbo prop" systems include; basic, intercooling, reheating, intercooling and reheating, regeneration, intercooling and reheating with regeneration, basic ducted fan, intercooling and reheating ducted fan, ducted fan with afterburing, basic ram jet, scream jet, liquid metal cycle nuclear turbo-jet, liquid metal cycle nuclear turbo-prop, ducted rocket and the like.

Applicant has found that ram jet and pulse jet operation represent a particularly preferred embodiment of this invention. Thus, Applicant incorporates by reference the thermal dynamics of the pulse jet. See, "Jet, Rocket, Nuclear, Ion and Electric Propulsion: Theory and Design," Edited and Authored by W.H.T. LOH, 1968, p 191.

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The desired combustion chambers of Applicant's turbine combustors include tubular, turbo-annular, annular type, and spherical.

Applicant's invention has particular application with the above turbine combustion configurations and systems in that it unexpectedly and significantly reduces the formation of free carbon in the primary combustion zone. It has also been found that the reduction of free carbon in the primary combustion zone, in turn reduces flame radiation, which in turn reduces combustion liner temperatures. Thus, reducing liner heat loads and increases engine life.

Furthermore, Applicant's reduced combustion temperatures are extremely useful for high altitude and high mach applications where extreme engine temperatures limit the operation and design of the combustion system. It has been found that Applicant can reduce engine combustion temperatures significantly, on the order of 25°F to 400°F, or more.

#### Example 36

A method of operating high altitude, high mach or other jet engine exposed to high operating temperature wherein said method comprises: Mixing an ECS fuel (containing an ECS compound and appropriate metallic) in such proportions with an aviation co-fuel that combustion at high mach or at extreme altitude is at reduced temperature; operating jet engine at high mach or at



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extreme altitude; wherein engine and combustion temperature is reduced 25°f to 300°F, 50°f to 350°F, 75°f to 375°F, 100°f to 400°F, 125°f to 450°F, 150°f to 500°F, 175°f to 550°F, 200°f to 600°F, 225°f to 750°F, 250°f to 900°F, or more.

5           It has also been found that Applicant's invention increases useful work, thrust, engine thermal efficiency from 0.5% to 2.0%, 0.5% to 5.0%, 1.0% to 10.0%, 5.0% to 20%, 10% to 40%, or more, and often quiet a bit more depending upon concentrations of the ESC fuel, the  
10 composition of the co-fuel, and the specific operation.

          Applicant's invention, in the application of jet turbines, also has particular advantage in reducing hazardous exhaust concentrations of CO, NOx and HC  
15 emission's, which are typically associated with idle condition.

          As noted above, problematic turbine coating manganese oxides, which have in the past plagued the usage of manganese in turbine fuels are now quite unexpectedly controlled. Applicant's reduction of combustion  
20 temperatures also beneficially reduces the coating of other compounds to turbine surfaces and reduces corrosion.

          In the practice of this invention, a preferred chemical means employing an ECS compound comprises a combustion improving amount of dimethyl carbonate in  
25 combination with a combustion improving amount of a cyclomatic manganese tricarbonyl compound in a base aviation jet turbine fuel. It is preferred that the final combination fuel be constructed to meet minimal ASTM

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specifications, including flash point, pour point, thermal stability, distillation, aromatic, density, freezing point, viscosity, net heat of combustion, and the like.

5 The hydrocarbon portion of the turbine fuel composition (co-fuel) comprises paraffins, naphthenes, olefins, and aromatics in order of their preference.

10 It is contemplated that the oxygen derived from ECS compounds fuels will be incorporated into aviation turbine fuels in varying concentrations, with optimal amounts dependent upon average flight altitudes, speed, lift/thrust requirements, combustion system configurations, combustion efficiencies, base fuel hydrocarbon composition, manganese concentrations, and the like.

15 Assuming an ECS oxygenated means of improving combustion, the recommended O<sub>2</sub> weight percentage concentration of the resultant fuel at sea level to 10,000 feet is from 0.1% to 5.0%, with 3.0% to 5.0% preferred; at 20,000 feet, the recommended O<sub>2</sub> weight percentage 0.1% to 10.0%, with 3.0% to 8.0% being preferred; at 30,000 feet  
20 the recommended O<sub>2</sub> weight percentage concentration is from 0.1% to 16.0%, with 5.0% to 7.0% recommended and 5% to 16.0% preferred; at 40,000 feet the recommended O<sub>2</sub> weight percentage concentration is from 0.1% to 30.0%, with 11.0% to 30.0% preferred. Recommended average O<sub>2</sub> weight percentage  
25 concentration of the resultant fuel may greatly exceed the upper limit of 30.0% or more, particularly in advanced fuel applications, extreme high altitudes, with fuel mixes containing alternative oxidants.

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Recommended average O<sub>2</sub> weight percentage concentrations of aviation turbine compositions for general distribution, involving co-fuel application, is from about 0.01% to about 3%, 1.0% to about 4.0%, 1.0% to about 7.0%, oxygen by weight of resultant fuel. 2.0% weight is an acceptable concentration. However, 4.5% weight percent is an average preferred concentration. Specific weight percentages of O<sub>2</sub>, in co-fuel applications, will vary with any particular fuel, its combustion system, flash point considerations, and operating conditions.

Manganese concentrations will range from 0.001 grams to 10.0 grams per gallon for aviation jet turbine fuel. However, concentrations substantially above this range is anticipated in advanced minority, majority, and/or neat ECS fuel applications. Hypergolic applications also dictate higher concentrations of Mn.

It also appears the higher the altitude of operation, the greater the indicated concentration levels of Mn. Higher concentration levels of manganese are permissible with higher concentrations of oxygen in the composition. As noted, higher concentrations of Oxygen are also indicated at higher altitudes. For example, operating at approximately 40,000 to 50,000 feet above sea level, acceptable Mn concentrations can range from about 0.001 to 4.00 grams/gal. At lower altitudes of approximately 5,000 to 20,000 feet above sea level, desirable Mn concentrations range from about 0.001 to 0.50 grams per gallon (those ranging from about 0.125 to 0.50 grams Mn/g

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being more desirable). However, concentrations outside these ranges are expressly contemplated, especially in more advance operations.

5 As in the practice of this invention elsewhere, metallic and oxygen concentrations are determined by optimizing the combustion of the composition, in the operating environment of the system.

Example 37

10 An aviation jet turbine fuel meeting ASTM 1655 specifications, diisopropyl ether or dimethyl carbonate, and mixture, representing 0.5% to 4.5%, 1.0% to 2.0% oxygen weight percent of the composition, and 1/64 to 1/8 g/gal Mn of a cyclopentadienyl manganese tricarbonyl compound.

15

Example 38

An aviation jet turbine fuel meeting ASTM 1655 specifications, diisopropyl ether and/or dimethyl carbonate, or mixture, representing 0.5% to 20.0% oxygen  
20 weight percent of the composition, and 0.001 to 5.0 g/gal Mn of a cyclopentadienyl manganese tricarbonyl compound.

Example 39

25 Same as examples 38, except that fuel is combusted in an aviation jet engine operating at 5,000 feet altitude above sea level.

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Example 40

Same as example 38, except the composition is combusted in an aviation jet engine which is operating at 20,000 feet altitude above sea level.

5

Example 41

Same as example 38, except dimethyl carbonate is in the composition at 25% oxygen weight percent and the cyclopentadienyl manganese tricarbonyl compound has a Mn weight in excess of 1.0 gr/gal.

10

Example 42

Same as example 38, except the composition is combusted in an aviation jet engine which is operating at 40,000 feet altitude above sea level.

15

Example 43

The examples of 38, wherein the dimethyl carbonate is in the composition at an oxygen weight of about 0.1 to about 3.0 percent.

20

Example 44

The examples of 37-43, wherein the composition contains ethylene glycol monomethyl ether in a concentration of 0.1 to 0.15% volume.

25

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Example 45

The examples of 38, wherein said operation is at altitudes in excess of 60,000 feet above sea level, wherein O<sub>2</sub> wt of DMC is 3.0% to 15.0% and metallic is a concentration of 0.5 to 10.0 grams/gal; whereby engine temperatures are reduced a minimum of 10°F to 400°F, or more, over known convention methods.

Example 46

A method of operating a high altitude jet engine comprising: mixing an aviation jet fuel with an ECS component representing 0.01 to 30.0% oxygen by weight of the composition together with a combustion improving amount of a high energy releasing metallic; operating said engine at altitude in excess of 40,000 feet, preferably 60,000 to 100,000 feet or more; exhausting combustor gases into inlet of a turbine; whereby gas inlet temperature is reduced below 1200°K., or best known method, by at least 0.5% to 25.0%, or more; and/or turbine inlet pressure is increased over existing methods by 0.5% to 40.0%; and/or thermal efficiency is improved by at least 0.5% to 20%, or more, over existing methods.

Example 47

An aviation jet turbine fuel meeting ASTM 1655 specifications containing an oxygenated ECS compound, wherein resultant fuel composition contains 0.5 to 4.0%

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oxygen weight percent, and at least one cyclopentadienyl manganese tricarbonyl compound at 1/8 gr Mn/gal.

Example 48

5           In combination, an aviation jet turbine engine and a jet turbine fuel meeting ASTM 1655 specifications containing an oxygenated ECS compound, wherein resultant fuel composition contains 0.5 to 5.0% oxygen weight percent, and at least one cyclopentadienyl manganese  
10       tricarbonyl compound at 1/8 gr Mn/gal, whereby the formation of free carbon in the primary combustion zone is reduced and inlet temperatures are substantially reduced.

Example 49

15           The combination of example 48, wherein combustion temperatures are reduced, or liner heat loads are reduced and/or turbine engine life is extended.

Example 50

20           The combination of example 48, wherein thermal efficiency is increased at least 2.0%

          Thus, it is an embodiment of this invention to employ Applicant's advanced ECS based fuel in combination with advance combustors having shorter combustor length to  
25       casing diameter ratios than convention combustors; reduced specific fuel consumptions with smaller diameter casting; smaller casing diameters with lower pressure losses, at higher combustion pressures; higher combustion pressure

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combustors absent increased turbine inlet or liner temperatures; reduced flame tubes sizes that do not sacrifice combustion efficiency, lift, or fuel economy; low pressure lift combustors of reduced flame tubes sizes that do not sacrifice combustion efficiency, lift, or fuel economy; larger diameter combustor casings that enjoy improved lift; larger diameter combustor casings with shorter flame tubes enjoying improved combustion efficiencies; reduced casing diameters absent increasing pressure losses; combustors having reduced pressure losses; lower compression ratio engines; lower compression ratio lift engines; higher compression ratio engines, absent adverse flame tube wall temperature increases (hence reducing film air cooling requirements); combustors wherein primary zone combustion efficiency is higher than conventional efficiencies; combustors wherein primary zone is lean or for fuel weak combustion; and the like.

Example 51

In combination, an ECS based aviation jet turbine fuel and a jet engine, the combination characterized by: the combustion of said fuel in a low pressure lift engine, wherein said engine's flame tube length has been decreased by at least 10%, absent impairing lift or combustion efficiency.



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Example 52

In combination, an ECS based aviation jet turbine fuel and a jet engine, the combination characterized by: the combustion of said fuel in a high compression engine, wherein said engine's turbine flame tube wall temperatures are reduced and thermal efficiency is increased by at least 5%.

It is an express embodiment of this invention to employ Applicant's combustion improving fuel compositions in combination with traditional or advanced aviation jet turbines combustors, which at high altitudes, including those in excess of 40,000 feet, enjoy improved combustion efficiencies 5% or better, than the co-fuel operating at the same altitude and/or at sea level.

It is an additional embodiment of this invention to reduce the total distance of the combustor's dilution zone, while simultaneously reducing the outlet stream temperatures. Thus, in the practice of this invention desirable dilution zone length is equal to 1.5 to 2.0 times the flame tube width, especially in engines intended for high altitude cruise. Other desirable dilution zone lengths are equal to 0.9 to 1.5, 1.2 to 1.6, 1.3 to 1.7, 1.4 to 1.6, times the flame tube width.

Thus, it is an embodiment of this invention to employ combustors whose dilution zone length is 1.4 to 1.6 times the total flame tube width, while at the same time improving combustion efficiencies at high altitudes.

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Contemplated combustion efficiencies are greater than 2% at altitudes in excess of 20,000 feet.

In order to prevent local damage to turbine blades, it is a further embodiment of this invention to construct ECS fuel and operate jet combustor such that the outlet stream temperatures (turbine inlet temperatures) be less than 1200°K.

Thus it is a further embodiment to operate such systems at turbine inlet temperatures no greater than approximately 1200°K, 1100°K, 1050°K, 1000°K, 950°K, 900°K, 850°K, or less. It is also an embodiment to operate said system at temperatures below 800°K, or less, if practical.

However, to maximize the benefits of Applicant's invention, it is desirable that maximum outlet stream temperatures of the combustor (e.g. maximum turbine entry temperatures) not exceed 1100°K. It is also preferred that the average/mean gas temperatures approximate the maximum turbine entry temperature, in order to maintain effective power out put of the engine.

#### Example 53

A method of reducing specific fuel consumption, comprising combusting an ECS fuel and/or an ECS plus co-fuel combination in an annular, tubular or turbo-annular combustor whose dilution zone length is about 1.5 times the flame tube width; whereby specific fuel consumption is reduced.

Example 54

The annular combustor examples of 53, wherein combustor length to casing diameter is reduced and wherein lift and/or fuel efficiency is improved of known methods.

5

Example 55

The examples of 53 and 54, wherein the ECS fuel comprises an majority ASTM aviation jet fuel and a minority comprised of dimethyl carbonate together with a combustion improving amount of at least one non-leaded metallic.

10

Example 56

The examples of 53-54, wherein the combustor operates on a hydrocarbon fuel composition containing a majority fuel component hydrocarbons and a minority comprising of dimethyl carbonate and a combustion improving amount of at least one cyclomatic manganese tricarbonyl, wherein outlet stream temperatures are less than 1100°K..

15

Example 57

The examples of 53-54, wherein the combustor operates on essentially a neat fuel composition comprising dimethyl carbonate and a combustion improving amount of at least one non-leaded metallic or.

20

Example 58

The example of 57, wherein the fuel composition additionally comprises a commercial jet aviation fuel co-fuel.

5

Example 59

The examples of 53-58, wherein usable work is increased and combustor life is extended by at least 10%.

10 Example 60

The combustor of examples 51-59, wherein combustion efficiencies at altitudes in excess of 30,000 feet are 2% greater than current engines.

15 Example 61

The combustor of examples 59-60, wherein pressures realized and/or turbine rotational speeds achieved are 5% to 20% greater than existing engines.

It is contemplated that Applicant's resultant and/or  
20 co-aviation turbine fuels will be lead free or essentially lead free. However, known additives consistent with ASTM, military, or International standards may be contained in the composition. It is contemplated that Applicant's aviation turbine fuel will meet or substantially comply  
25 with ASTM standards. Current ASTM fuel specification D 1655-93 (including future editions), relevant prior specifications, related ASTM standards, test methods,

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military, and international standards are incorporated by reference.

5 The anti-oxidants of Applicant's invention include alkyl phenol and aromatic diamines with sterially hindered phenolic and amine groups.

Applicant's anti-oxidants are normally used in amounts not to exceeding 24.0 mg/L active ingredients (not including weight of solvent). Such antioxidants are selected from N,N-diisopropylparaphenylene diamine, 10 seventy-five percent minimum 2,6-di-tertiary-butyl phenol plus 25% maximum tertiary and tritertiary butyl phenols, seventy-two percent minimum 2,4-dimethyl-6-tertiary-butyl phenol plus 28% maximum monomethyl and dimethyl tertiary-butyl phenols, fifty-five percent minimum 2,4-dimethyl-6- 15 tertiary-butyl phenol plus 45% maximum mixed tertiary and ditertiary butyl phenols.

Additional anti-oxidants that may be employed in this invention include 2,6-di-tert-butyl-4-methylphenol, 6-tert-butyl-2,4-dimethylphenol, 2,6-di-tert-butylphenol, 75 20 percent min-2, 6-di-tert-butylphenol 25 percent max tert-butylphenols and tri-tertbutylphenols, 72 percent min 6-tert-butyl-2, 4-dimethylphenol 28 percent max tert-butyl-methylphenols and tert-butyl-dimethylphenols, 55 percent min 6-tert-butyl-2, 4- 25 dimethylphenol 45 percent max mixture of tert-butylphenols and ditert-butylphenols, 60 to 80 percent 2,6-dialkyphenols 20 to 40 percent mixture of 2,3,6-trialkylphenols and 2,4,6-

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trialkylphenols, 35 percent min 2,6-di-tert-butyl-4-methylphenol 65 percent max mixture of methyl-, ethyl-, and dimethyl-tert-butylphenols, 60 percent min 2,4-di-tert-butylphenol 40 percent max mixture of tert butylphenols, 30 percent min mixture of 2,3,6-trimethylphenol and 2,4,6-trimethylphenol 70 percent max mixture of dimethylphenols, 55 percent min butylated ethylphenols 45 percent max butylated methyl- and dimethylphenols, 45 percent mix 4,6-di-tert-butyl-2-methylphenol, 40 percent min mixture of 6-tert-butyl-2-methylphenol 15 percent max mixture of other butylated phenols. Also inhibitors whose total concentration is not greater than 1.0 lb, not including weight of solvent, per 5000 gal of fuel, of: 2, 4-dimethyl-6-tertiary-butyl phenol, 2, 6-detertriary-butyl-4-methyl phenol, 2, 6-ditertiary-butyl phenol, 75% 2, 6-ditertiary-butyl phenol, 10-15% 2, 4, 6-tritertiary-butyl phenol, 10-15% orthy-tertiary butyl phenol, 72% min 2, 4-dimethyl-6-tertiary butyl phenol, 28% max. monemethyl and dimethyl tertiary butyl phenol, 60% min 2, 4-ditertiary-butyl phenol, 40% max, mixed, tertiary-butyl phenol. Additive concentrations outside these limits are contemplated, particularly in other applications of the invention and/or where the nature or concentration of ECS compounds warrant such usage.

25           The composition may contain metal deactivators, in a preferred amount not to exceed about 5.8 mg/L (not including weight of solvent), such as N,N<sup>1</sup>-disalicylidene-1,2-propane diamine, N,N<sup>1</sup>-disalicylidene-1,2-ethane diamine

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or N,N<sup>1</sup>-disalicylidene-1,2-cyclohexanediamine. However, concentrations outside this amount is contemplated.

Electrical Conductivity Additives, in sufficient concentration to increase the conductivity of the fuel to within the range of 200 to 600 picosiemens per meter at the point of injection, such as ASA-3 (marketed by Royal Lubricants Corp., Roseland, NJ 07068) in concentrations up to 1 mg/L, and "Stadis" 450 (registered trademark and marketed by DuPont Petroleum Chemicals Div., Wilmington, DE 19898) in concentrations up to 3 mg/L are expressly contemplated.

In the practice of this invention, when loss of fuel conductivity necessitates retreatment with electrical conductivity additives the following concentration limits apply: ASA-3 @ 1 mg/L, max; Stadis® 450 @ 3 mg/L, max. When retreatment using the same conductivity additives is necessary concentration limits for ASA-3 is limited to an accumulative total of 2 mg/L, max; and for Stadis® 450 an accumulative total of 5 mg/L, max. When a retreatment is desired due to a change of conductivity additive or when identity is unknown ASA-3 may be further added but not to exceed 1 mg/L, max; Stadis® 450 may be further added but not to exceed 2 mg/L, max.

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Corrosion inhibitors are contemplated. For example, the following anticorrosive additives may be employed:

	ADDITIVE	CONCENTRATION
5	Nuchem PCI-105	4 lb per 1000 BBL maximum.
	Apolio PRI-19	4 lb per 1000 BBL maximum.
10	Cooper Hiteo E-515	16 lb per 1000 BBL maximum.
	Cooper Hiteo E-580	8 lb per 1000 BBL maximum.
15	DuPont AFA-1	16 lb per 1000 BBL maximum.
	Petrolite	20 lb per 1000 BBL maximum.
20	Tolad 245	
	Texaco TXA182	20 lb per 1000 BBL maximum.
25	(TRI 182)	

Other suitable corrosion inhibitors may employed. In the case of military applications a corrosion inhibitor conforming to MIL-I-25017 may be blended into the JP-8 grade fuels.

The practice of this invention expressly contemplates the usage of a fuel system icing inhibitor, especially in circumstances where required to reduce freezing temperatures. The freezing point is particularly important and must be sufficiently low to preclude interference with flow of fuel through filter screens to the engine at temperatures prevailing at high altitudes. The temperature of fuel in an aircraft tank decreases at a rate proportional to the duration of flight. The maximum freezing point allowed for the fuel is therefore related to



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the type of flight. For example, long duration flights would require fuel of lower freezing point than short duration flights.

5 A preferred icing inhibitor is ethylene glycol monomethyl ether, conforming to the requirements of Specification D 4171. Preferred concentrations range from about 0.1 to 0.15 volume %. However, concentrations outside this range may be employed. Additional anti-icing additives include Phillips PFA 55 MB @ 0.15% Vol. and MIL-I-27686 @  
10 0.15% Vol. Max.

In the practice of this invention, it is contemplated that additional icing inhibitors may be employed, including alcohols, co-solvents, and the like, especially where the ECS compound does not have a sufficiently low melting point  
15 and/or when the finished fuel's pour point or freeze temperature is too high.

The fuel specifications of Applicant's jet aviation turbine fuels shall generally comport to requirements of TABLE 1.

20 It is preferred that Applicant's aviation turbine co-fuel shall generally be visually free of undissolved water, sediment, and suspended matter. The odor of the fuel shall not be nauseating or irritating. No substance of known dangerous toxicity under usual conditions of handling and  
25 use shall be present, except as set forth herein.

The safe and economical operation of aircraft requires that Applicant's fuel be essentially clean, dry and free of any contamination prior to its use.

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Thus, Applicant's aviation jet turbine co-fuels should

be free of water and/or otherwise be anhydrous. However, in certain circumstances, water may be incorporated into the

5 fuel, for example via an emulsion or other means, for example by separate injection, to increase burning velocity and/or vapor diffusion.

**TABLE 1**  
**Representative Requirements of Aviation Turbine Fuels<sup>A</sup>**

5	Property		Jet A or Jet A-1	Jet B	ASTM Test Method
	<b>COMPOSITION</b>				
	Acidity, total mg KOH/g	max	0.1	...	D3242
	Aromatics, vol %	max	22 <sup>C</sup>	22 <sup>C</sup>	D1318
10	Sulfur, mercaptan, weight %	max	0.003	0.003	D3227
	Sulfur, total weight %	max	0.3	0.3	D1266 or D1662 or D2622 or D4284
	<b>VOLATILITY</b>				
	Distillation temperature, °C				
15	10% recovered, temp	max	205	...	D86
	20% recovered, temp	max	...	145	
	50% recovered, temp	max	report	190	
	90% recovered, temp	max	report	245	
	Final boiling point, temp	max	300	...	
20	Distillation residue, %	max	1.5	1.6	
	Distillation loss, %	max	1.6	1.5	
	Flash point, °C	min	38	...	D56 or D3828 <sup>I</sup>
	Density at 15°C, kg/m <sup>3</sup>		775 to 840	761 to 802	D1298 or D4052
	Vapor pressure, 38°C, kPa	max	...	21	D323
25	<b>FLUIDITY</b>				
	Freezing point, °C	max	-40 Jet A <sup>E</sup> -47 Jet A-1 <sup>E</sup>	-50 <sup>B</sup>	D2388
	Viscosity -20°C, mm <sup>2</sup> /s <sup>L</sup>	max	8.0		D445
30	<b>COMBUSTION</b>				
	Net heat of combustion, MJ/kg	min	42.8 <sup>G</sup>	42.8 <sup>G</sup>	D4529, D3338 or D4809
35	One of the following requirements shall be met:				
	(1) Luminometer number, or	min	45	45	D1740
	(2) Smoke point, mm, or	min	25	25	D1322
	(3) Smoke point, mm, and	min	19 <sup>F</sup>	19 <sup>F</sup>	D1322
	Naphthamines, vol, %	max	3	3	D1840
40	<b>CORROSION</b>				
	Copper strip, 2 h at 100°C	max	No. 1	No. 1	D130
45	<b>STABILITY</b>				
	Thermal:				
	Filter pressure drop, mm Hg	max	25 <sup>K</sup>	25 <sup>K</sup>	D3241 <sup>H</sup>
	Tube deposit less than		Code 3	Code 3	
	No Peacock or Abnormal Color Deposits				
50	<b>CONTAMINANTS</b>				
	Existent gum, mg/100 mL	max	7	7	D381
	Water reaction:				
	Interface rating	max	1b	1b	D1094
55	<b>ADDITIVES</b>				
	Electrical conductivity, pS/m		See 5.2	See 5.2	D2524

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It is preferred that Applicant's aviation turbine co-fuel be thermally stable at temperature as high as 300°F, in order to reduce the amount of deposits formed in the engine fuel systems when heating the fuel. Thermal stability is an important property of aviation jet turbine fuels and potentially effects both maintenance and operability of the engine. Deposits can plug fuel nozzles, reduce efficiency of heat exchangers and cause malfunctioning of fuel controls. Thus, the ECS compound employed should not adversely affect thermal stability. However, ECS compound effecting thermal stability may be employed, if appropriate counter measures, such as appropriate additives (see below) and/or certain formulation techniques. See Aviation Fuel: Thermal Stability Requirements, Perry W. Kirklin and Peter David, 1992.

It is preferred, for example that the resultant fuel's high temperature stability property be measured in the ASTM-C8C Fuel Coker after five hours of operation of 300°F (148.9°C) preheater temperature, 400°F (204.4°C) filter temperature and six pounds per hours ( $2.70 \pm 0.05$  Kg/hr) fuel flow rate. Preferred maximum pressure change is 12 inches (304.8 mm) Hg. max, and preheater deposit is less than Code 3 (ASTM 1660). Such fuels will have inherent storage stability, as well.

Thus, in the practice of this invention it is contemplated that Applicant's fuels, in order to improve thermal stability, will employ fuel production methods

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and/or processes which remove to the extent possible reactive olefins and heteroatom compounds.

It is also contemplated the fuel may contain an additives for thermal stability including, DuPont's JFA-5  
5 in concentrations of 30 lb per 1000 BBL, maximum. Additional additives, which are in conformity with ASTM D 1655 are also contemplated.

Applicant's preferred fuel composition is formulated to elicit combustion characteristics that reduce soot  
10 formation, increase burning efficiency and avoid flame-out.

In general, paraffin hydrocarbons offer the most desirable combustion cleanliness characteristics for jet fuels. Naphthenes are the next most desirable hydrocarbons for this use.

15 Although olefins generally have good combustion characteristics, their poor gum stability and thermal stability characteristics usually limits their use in aircraft turbine fuels. In the practice of this invention their usage should be limited to 5% by volume or less.  
20 However, volumes of 1% or less, are more preferred.

Absent Applicant's invention, aromatics generally have the least desirable combustion characteristics for aircraft turbine fuel. In aircraft turbines, they tend to burn with a smoky flame and release a greater proportion of their  
25 chemical energy as undesirable thermal radiation than the other hydrocarbons. Naphthalenes or bicyclic aromatics produce more soot, smoke, and thermal radiation than monocyclic aromatics and are, therefore, the least

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desirable hydrocarbon class for aircraft jet fuel use.

It is preferred that the luminometer number of Applicant's composition, which measures the radiation from and temperature rise in a flame under prescribed conditions and is related to the hydrocarbon-type composition of the fuel, be a minimum of 45.

It is preferred that the smoke point, which is an indication of the relative smoke-producing properties of jet fuels and is related to the hydrocarbon-type composition of the fuel, be a minimum of 25 mm. Generally, the more highly aromatic the jet fuel, the more smoky the flame.

It is also preferred that naphthalenes represent not more than 3.0 volume percent of the composition. Naphthalene concentrations lower are more preferred. For purposes of this invention naphthalene shall include naphthalene, acenaphthene, and alkylated derivatives of these hydrocarbons in jet fuels containing no more than 5% of such compounds and having boiling points below 600°F (316°C). Naphthalene concentrations below 3% are preferred. Lower naphthalene concentrations are even more preferred.

It is preferred that aromatic volume concentrations be less than 22% by volume. Maximum aromatic concentrations in kerosene fuels should be 20% or less. Lower concentration are preferred. Absent the application of instant invention, the combustion of highly aromatic jet fuels generally results in smoke and carbon or soot deposition.

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The hydrogen content of the fuel is also an important element of applicant's invention. In the practice of Applicant's invention it is desirable that total hydrogen as a percent of mass of the fuel not be less than 13.4% mass. Preferred concentrations are 13.8% mass. More preferred exceed 14.0% mass. Hydrogen concentrations outside these ranges are contemplated. The fuel's density is a property of significance in metering flow and in mass-volume relationships for most commercial transactions. Thus, Applicant's fuel should be constructed to flow easily in normal operating circumstances. The fuel's density is particularly useful in empirical assessments of heating value when used with other parameters such as aniline point or distillation. A low density may indicate low heating value per unit volume. The preferred density of Applicant's jet aviation fuel shall range from approximately 750 to 840 kg/m at 15°C.

Likewise, Applicant's fuel's net heat of combustion, which effects the aircraft and its engines, is based on the convertability of heat into mechanical energy. As noted, net heats of combustion are higher in the preferred practice of this invention.

However, a minimum net heat is an essential embodiment of this invention. It is contemplated the minimum net heat of combustion be 42.8 MJ/kg. Higher net heats of combustion including those in excess of 43.0 MJ/kg are also acceptable and often preferred. However, the unexpected capacity of Applicant's invention to convert heat into mechanical

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energy permits the use of net heats below 42.8 MJ/kg, especially when the ESC component increases volumetrically in the composition.

5 The fuel's volatility and ease of vaporization at different temperatures are determined by distillation. The 10% distilled fraction should ensure easy starting. The 90% fraction should limit heavier fractions that would be difficult to vaporize. Preferred T-90 temperatures should not exceed 250°C, however lower temperatures are slightly  
10 more preferred.

The fuel's vapor pressure should be sufficient to avoid foaming, fuel slugging, and losses of light ends through aircraft tank vents at high altitude. This is of significance with respect to Jet B fuel because of its  
15 higher volatility.

Viscosity of a fluid is a measure of its resistance to flow. In turbine fuels it is highly significant since it indicates both the relative ease with which the fuel will flow or may be pumped, and the ease of atomization by the  
20 fuel nozzles. Minimum viscosity is limited because some fuel pumps will not perform satisfactorily if the viscosity reaches too low a value, especially in cold temperature conditions. Maximum viscosity is limited since too high a viscosity can cause excessive pressure losses in the piping  
25 system, and poor fuel atomization. Thus, the preferred viscosity of Applicant's fuel should be sufficient to insure pumpability over expected operational temperature ranges and be consistent with nozzle spray patterns.



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A limitation in mercaptan content is desirable to preclude adverse reactions with elastomers and to minimize the unpleasant mercaptan odor. In the practice of this invention, the fuel's preferred mercaptan sulfur weight% is

5 0.003 or less.

In the practice of this invention it is desirable to limit sulfur content because sulfur oxides formed during combustion are corrosive to jet turbine metal parts. It is preferred that sulphur weight% is 0.3, 0.2 to 0.001 (or

10 sulphur free).

In the practice of this invention, the fuel's preferred copper strip corrosion number, 2 h at 100°C, shall not exceed No.1. This will insure that the fuel will not corrode copper or any copper-base alloys in various parts

15 of the fuel system.

Reduction of acidity is important to avoid potential hydrolysis of certain oxygenates, avoid corrosion and/or materials incompatibility, and/or to avoid thermal stability problems. Thus, any residual mineral acid,

20 caustic, acid, or acidic forming material/agent should be removed or eliminated from the process. If acidic or acid forming ECS compounds are employed anti-oxidant and/or neutralizing additives are contemplated. In the practice of this invention, it is preferred that the acidity of

25 Applicant's fuel be minimized and not exceed 0.1 mg KOH/g.

It is also preferred that existent gum, a nonvolatile residue left on evaporation of fuel, be minimized. Large quantities of gum are indicative on contamination of fuel

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by higher boiling oils or particulate matter and generally reflect poor fuel handling practices.

Applicant's preferred jet aviation fuel is usable after storage for variable periods under a variety of climatic conditions, and should meet applicable ASTM requirements.

Applicant's desired flash point, an indication of the maximum temperature for fuel handling and storage without serious fire hazard, should be about 38°C or higher. However, fuels with lower flash points are expressly contemplated.

Flash point management is important in the practice of Applicant's invention. Should flash point temperatures be reduced by the addition of an ECS compound, it is expressly contemplated that a substitute ECS compound and/or supplement be employed to raise flash point temperature. Other means of achieving acceptable flash point temperatures are contemplated. For example, the co-fuel may be cut at higher flash point temperatures, so that the combined ECS compound and base fuel meet acceptable ASTM flash point temperatures. It has been found that reducing total concentration levels of certain lower flash point ECS compounds is also effective. Other additives, including salts, surfactants, and the like that increase flash point are contemplated. Co-solvent practice is also contemplated for flash point, vapor pressure, water solubility, hydrolysis, and other such problems (see EPO Patent # 0235280).

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It is generally preferred that the fuel be free of surfactants. However, in certain cases, for example as a means of creating an emulsion or raising flash point, surfactants may be used.

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An illustrative example of Applicant's ECS turbine aviation jet fuel is as follows:

	Properties	Limits	Limits	Test Method
5	Gravity, deg AFI	37	57	ASTM D287
	Distillation Temp., 10% evaporated	max	400°F (204.4°C)	
10	50% evaporated	190.2°C	450°F (232.2°C)	
	End Point	max	572°F (300°C)	
	Loss, %	max	1.5	
15	Residue, %	max	1.5	
	Sulfur, % by weight	max	0.30	ASTM D1266
	Mercaptan Sulfur, % by weight (See Note 1)	max	0.005	ASTM D1323 or D1219
20	Net Heat of Combustion			
	BTU/lb	18,400	min	ASTM D240
	J/Kg	42.8 x 10 <sup>6</sup>	min	D2382
25	Freezing Point, F (See Note 2)			
	Reid Vapor Pressure, lb m	5.0	3	ASTM D323
	Aromatic Content, % by volume (See Note 3)		20	ASTM D1319
30	Burning Quantity Luminometer # (See Note 4)	45	min	ASTM D1740
	Copper Strip Corrosion, Classification	max	40	ASTM D130
35	Temp: 100°C = ° 212°F = 1.8° Time: 2 hrs.			
	Viscosity, Cs at -30°F (-34.4°C)	max	15	ASTM D445
40	Water Reaction, Volume Change, ml	max	1	ASTM D1094
	Water Reaction, Interface Rating	max	1-b	ASTM D1094
45	ECS Fuel/Compound (O2 wt%, dimethyl carbonate)	2.0%		2.0%
50	CMT (g./gal)	1/8	1/16	

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Note 1. Mercaptan sulfur determination may be omitted provided Doctor test per ASTM D484 is conducted and results are negative.

5 Note 2. The freezing point shall be at least 6°F below the minimum engine fuel inlet temperature.

Note 3. May contain aromatic up to 25% by volume.

10 Note 4. Fuels will be acceptable provided they meet one of the following alternative requirements or combination of requirements:

15 a. Smoke point of not less than 25 mm when determined per ASTM Method D1322.

20 b. Smoke point of not less than 20 mm when determined per ASTM Method D1322 provided fuel does not contain more than 3.0 percent by volume of naphthalene as determined per ASTM D1840.

25 c. Due to occasional difficulties meeting the requirement of item b., minimum smoke point may be relaxed down to 18 mm, as necessary, when determined per ASTM method D1322, provided fuel does not contain more than 3.0 percent naphthalene as determined per ASTM D1840.

30

The use of aromatics and other means, presented herein, to modify distillation and volatility, while having certain applicability, are generally limited in the case of  
35 Jet A and Jet A-1 fuels. But, non-the-less may be applied in warranted circumstances.

Applicant notes, that while aromatic compounds have particular advantage in maintaining fuel stability and/or in modifying fuel volatility, their application in Jet A or  
40 Jet A-1 fuels for purposes of modifying temperatures are

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limited, because T-10 and end-boiling temperatures for said fuels vary only about 100°C.

While adverse conditions generally associated with aromatic usage, e.g. free carbon formation, are largely controlled by the practice of this invention, such aromatics, otherwise tend to aggravate flame radiation, smoke, and erode elastomers. Consequently, their usage to the extent possible, should be limited or avoided. However, it is an express embodiment to employ aromatics at concentrations outside those preferred, while still achieving measurable reductions in flame radiation, emissions, etc.

#### GAS TURBINE FUEL OILS AND SYSTEMS

Applicant's invention expressly contemplates gas turbine fuel oils and co-fuel application of gas turbine fuel oils, and the like, including those meeting suitable requirements of industry, gas oil turbine manufactures, ASTM D 2880 standards, and the like. ASTM fuel specifications D 2880-92, D 396 and D 975 (including future editions), relevant prior specifications, related ASTM standards, test methods, military, and international standards are incorporated by reference.

Applicant's gas turbine oil fuels also enjoy the same reduced carbon formation, reduced temperature, and higher thermal efficiency attributes as aviation jet turbines. Thus, unexpected reduction in radiant energy, inner liner temperature reductions, and consequential extension of gas

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oil turbine lives, is contemplated by this invention. Additionally, due to higher net heats a substantial improvement of usable power is also unexpectedly experienced.

5           In the practice of gas turbine fuels, as compared to aviation jet applications, emphasis is on combustion efficiencies, low pressure losses, long term durability, reduction of emissions over a wide range of fuels, including so called "dirty fuels," ash deposition and  
10           corrosion on turbine blading, and the like.

          The basic turbine combustion systems contemplated in Applicant's gas oil turbines, include those previously set forth above under aviation jet turbine systems and those other combustors employed in a wide range of industrial and  
15           marine power production applications.

          Thus, combustors, include diffusion flame, catalytic combustors, premixing combustors, and others. Applicant has found that catalytic combustors are desireable in the practice of this invention.

20           Unlike aviation turbines, weight and compactness are not as critical. Thus, the long term reliability and accessibility of larger single multi-head combustors are common.

          Thus, non-limiting examples of combustion/fuel system  
25           contemplated in this application include, combustors wherein primary zone is lean or for fuel weak combustion, turbo-charged marine turbine engines burning heavy bunker fuels, high temperature gas turbine with intermediate gas

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dilution, high temperature gas turbine with intermediate high temperature heat exchanger, high temperature gas turbine with intermediate heat exchanger and gas dilution, high temperature gas turbine with reheat, and the like.

5           The principal objects of Applicant's gas oil turbine fuel and combustion system are the improvement of thermal efficiency, reduction of harmful pollution, reduction of harmful ash deposits, and control of corrosion on turbine blading.

10           Non-limiting examples of the gas turbine fuel oils of this invention include four grades of fuel oils encompassed by ASTM Specifications D 396 and D 975. Included is a No. 0-GT grade, which covers low-flash naphthas. While there is a general similarity with fuels primarily intended for  
15           aircraft use, particularly kerosene usage, the fuels for Applicant's gas turbine fuel oil applications have some differences, which are set out below.

          However, the combustion principles of jet turbines and stationary gas oil turbines are similar. Thus, it is  
20           intended the practices and/or any relevant aviation jet turbine disclosure above, or the disclosure or any other fuel set forth, which may be applicable, be employed in the practice of Applicant's gas turbine fuel oils.

25           Example 62

          A gas turbine fuel oil composition comprising a minority portion of an ECS fuel, preferably comprising a combustion improving amount of dimethyl carbonate with a



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combustion improving amount of a non-leaded metallic or compound, and a majority portion of a gas oil turbine fuel, whereby resultant composition meets applicable ASTM D 2880, D 396, and D 975 standards, present and future.

5

Example 63

The example of 62, wherein the oxygen concentration of the resultant composition ranges from about 0.1% to about 20.0% by weight, a more preferred oxygen range being from 2.0% to about 6.0% weight percent, an even more preferred being 4.0% by weight.

10

Example 64

The example of 62, wherein end point or T-90 temperatures are reduced by 50°F, 100°F, 150°F, 200°F, such that combustion temperatures are reduced.

15

Example 65

The example of 62, wherein end point or T-90 temperatures are reduced by 50°F, 100°F, 150°F, 200°F, such that combustion temperatures are reduced in combination with the presence of an ESC compound.

20

Example 66

The example of 62, wherein the cyclomatic manganese compound is present in the composition in an amount from about 0.001 to 2.00 gram Mn/gal, with 0.001 to 0.50 g

25

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Mn/gal preferred, with 0.125 to 0.375 g Mn/gal more preferred.

Example 67

5           A gas turbine fuel oil composition comprising a majority portion of an ECS fuel, preferably comprising a combustion improving amount of dimethyl carbonate with a combustion improving amount of a cyclopentadienyl manganese tricarbonyl compound, and a minority portion of a gas oil  
10 turbine fuel, whereby resultant composition meets applicable ASTM D 2880, D 396, and D 975 standards.

Example 68

15           The example of 67, wherein the oxygen concentration of the resultant composition ranges from about 0.1% to about 50.0% by weight. Preferred oxygen ranges are from 6.0% to 40% weight percent of the composition.

Example 69

20           The example of 67, wherein the cyclomatic manganese compound is present in the composition in an amount from about 0.0625 to 3.00 gram Mn/gal, with 0.25 to 1.50 g Mn/gal preferred, with 0.125 to 0.375 g Mn/gal also preferred.

25

Example 70

          An ECS fuel and a co-fuel selected from the group consisting of No. 0-GT, No. 1-GT, No. 2-GT, No. 3-GT, or

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No. 4-GT gas turbine fuels, wherein the resultant fuel meets ASTM D 2880 specifications.

Example 71

An ECS fuel containing a combustion improving amount of a cyclopentadienyl manganese tricarbonyl compound, and a hydrocarbon co-fuel selected from a No. 0-GT, No. 1-GT, No. 2-GT, No. 3-GT, or No. 4-GT gas turbine fuel oil, wherein the oxygen content of the resultant fuel is 4.5% oxygen weight percent.

Example 72

The composition of example 71, wherein said composition meets ASTM D 2880 specifications.

Example 73

The composition of example 71, wherein said composition's end boiling point, T 90, and T-50 temperatures are reduced at least 10°F to 50°F, whereby combustion is improved and/or emissions are reduced.

Example 74

In combination, a fuel composition selected from the group consisting of a No. 0-GT, No. 1-GT, No. 2-GT, No. 3-GT, or No. 4-GT gas turbine fuel, a gas fuel oil turbine combustion system, said combination being characterized in that: said fuel contains a combustion improving amount of dimethyl carbonate and a combustion improving amount of a cyclopentadienyl manganese tricarbonyl compound; whereby

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carbon formation is reduced in the primary combustion zone, during combustion of said composition.

Example 75

- 5        The combination of example 74, wherein a fuel atomization means is employed, whereby the average fuel droplet size is less than 70 microns.

Example 76

- 10       The combination of example 74, wherein a fuel atomization means is employed, whereby the average fuel droplet size is less than 40-60 microns.

Example 77

- 15       The examples of 75-76, wherein free carbon formation is reduced such that inner liner temperatures are reduced with attendant increases in turbine life.

Example 78

- 20       The example of 74, wherein the combination further contains a means to reduce the composition's end boiling point, T 90, or T-50, or T-10 temperatures; whereby hazardous emissions are reduced.

25       Example 79

- The examples of 62-78, wherein the compositions are combusted in a gas turbine flame tube, and wherein the turbine inlet gas temperature is less than 650°C.

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Example 80

The examples of 62-78, wherein the compositions are combusted in a gas turbine flame tube, and wherein the turbine inlet gas temperature is less than 550°C.

5

Example 81

The examples of 62-80, wherein the compositions are combusted in a gas turbine flame tube (combustor) whose dilution zone length is 1.4 to 2.0 (1.4 to 1.6) times the total flame tube width, wherein the turbine inlet gas temperature is less than 650°C.

10

Example 82

The examples of 62-81, wherein the compositions are combusted in a gas turbine flame tube (combustor) whose dilution zone length is approximately 1.5 times the total flame tube width, wherein the turbine inlet gas temperature is less than 650°C, and wherein inlet pressures and/or turbine rotational speeds are increased 2% to 10% over existing systems.

15

20

Example 83

The examples of 62-82, wherein the compositions are combusted in a gas turbine flame tube such that turbine inlet gas temperature is about 550°C or less, and wherein inlet pressures and/or turbine rotational speeds realized are 2% to 10% greater than achievable using current compositions and combustors, under the same conditions.

25

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The physical properties of Applicant's co-fuel and resultant gas fuel oils are generally the same as those specified by ASTM Specifications D 2880, D 396 and D 975.

5 For example, gas turbine operating experience has shown that the ash content of fuels to be problematic. Thus, certain chemical properties of the fuel oil ash must be controlled since slag-forming substances present in the oil ash can cause corrosion and deposits on those turbine parts that must operate at surface temperatures of 593° and  
10 above. Low/no ash fuels are an express embodiment of this invention.

The various grades of ASTM gas oil turbines fuels noted above, include grades 0-GT through 4-GT. Grade 0-GT includes naphtha, Jet B, and other light hydrocarbon  
15 liquids that characteristically have low flash point and low viscosity as compared to kerosine and fuel oils. Grade 1-GT is a light distillate fuel oil suitable for use in nearly all gas turbines. Grade 2-GT, which is a heavier distillate than Grade 1-GT, can be used by gas turbines not  
20 requiring the clean burning characteristics of Grade 1-GT.

For Grade 2-GT, fuel heating equipment may be required depending on the fuel system design or ambient temperature conditions, or both.

Additional gas turbine fuel oil grades include: Grade  
25 3-GT, which may be a heavier distillate than Grade 2-GT, or a residual fuel oil that meets the low ash requirements, or a blend of distillate with a residual fuel oil. In the case

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of Grade 3-GT, fuel heating will be required in almost every installation.

Grade 4-GT includes most residuals and some topped crudes. Because of the wide variation and lack of control  
5 of Grade 4-GT properties, it is advisable to acceptable properties of such grade prior to use.

In the practice of this invention, different gas turbine fuels prepared to different specifications and sold under different names are acceptable. However, those that  
10 meet the requirements of fuels specified under ASTM Specification D 2880, are preferred.

Desireable gas turbine co-fuels of this invention are homogeneous mixtures of hydrocarbon oils, free of inorganic acid, and free of excessive amounts of solid or fibrous  
15 foreign matter, which would otherwise make frequent cleaning of suitable strainers necessary. It is preferred that all grades of turbine fuel oil remain homogeneous in normal storage and not separate by gravity into light and heavy oil components outside the viscosity limits for the  
20 grade.

Applicant's turbine fuel oils should be primarily hydrocarbons. It is also preferred that Applicant's co-fuel turbine fuel oils be free of contaminants. In the present  
25 context, contaminants are considered to be foreign materials that make the fuel less suitable or even unsuitable for the intended use.

The various grades of gas turbine fuel oil contemplated in Applicant's invention shall conform to the

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limiting requirements shown in Table 2. The requirement for Grade No., 1-GT and 2-GT conform in most respects to the corresponding Grade Nos. 1 and 2 fuels of ASTM Specification D 396, and to Grade Nos. 1-D and 2-D in ASTM Specification D 975. The viscosity range of Grade Nos. 3-GT and 4-GT fuel brackets the Grade Nos. 4, 5, and 6 of ASTM Specification D 396 and Grade No. 4-D of ASTM Specification D 975.

It is the intent of this invention that fuels meeting ASTM Specification D 396 and D 975 requirements be employed. Non-limiting examples of acceptable fuels include fuels meeting the requirements of Table 2.



**TABLE 2**  
**DETAILED REQUIREMENTS FOR GAS TURBINE FUEL OILS AT TIME AND PLACE**  
**OF CUSTODY TRANSFER TO USER<sup>A,B</sup>**

5	Property	ASTM Test Method <sup>C</sup>	Grade <sup>D</sup>				
			No. O-GT	No. 1-GT	No. 2-GT	No. 3-GT	No. 4-GT
	FLASH POINT	D 93	<sup>E</sup>	38 (100)	38 (100)	65 (130)	66 (150)
	°C (°F) min						
10	WATER AND SEDIMENT	D 1798	0.05	0.05	0.05	1.0	1.0
	% vol max						
	DISTILLATION						
	TEMPERATURE	D 86					
	°C (°F)						
15	90% VOL. RECOVERED						
	min		...	...	282	...	...
	max		...	288	338	...	...
	KINEMATIC VISCOSITY						
20	2 mm/g <sup>F</sup>	D 445					
	AT 40 °C (104 °F) min		<sup>G</sup>	1.3	1.9	5.5	5.5
	max			2.4	4.1	...	...
	AT 100 °C (212 °F) max			...	...	50.0	50.0
	RAMSBOTTOM						
25	CARBON RESIDUE	D 524	0.15	0.16	0.35	...	...
	on						
	10% DISTILLATION						
	RESIDUE						
	% mass, max						
30	ASH						
	% MASS, max	D 482	0.01	0.01	0.01	0.03	...
	DENSITY at						
	15 °C kg/m <sup>3</sup>						
	max		...	850	876	...	...
35	POUR POINT <sup>F</sup>	D 97	...	-18	-6	...	...
	°C (°F) max						

<sup>A</sup> To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

<sup>B</sup> Gas turbines with waste heat recovery equipment may require fuel sulfur limits to prevent cold and corrosion. Environmental limits may also apply to fuel sulfur in selected areas in the United States and in other countries.

<sup>C</sup> The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 6.1.

<sup>D</sup> No. O-GT includes naphtha, Jet B fuel and other volatile hydrocarbon liquids. No. 1-GT corresponds in general to specification D 396 Grade No. 1 fuel and D 975 Grade 1-D diesel fuel in physical properties. No. 2-GT corresponds in general to specification D 396 No. 2 fuel and D 975 Grade 2-D diesel fuel in physical properties. No. 3-GT and No. 4-GT viscosity range brackets specification D 396 Grades No. 4, No. 5 (light), No. 5 (heavy), and No. 6, and D 975 Grade No. 4-D diesel fuel in physical properties.

<sup>E</sup> When the flash point is below 38 °C (100 °F) or when kinematic viscosity is below 1.3 mm<sup>2</sup>/s at 40 °C (104 °F) or when both conditions exist, the turbine manufacturer should be consulted with respect to safe handling and fuel system design.

<sup>F</sup> For cold weather operation, the pour point should be specified 6 °C below the ambient temperature at which the turbine is to be operated except where fuel heating facilities are provided. When a pour point less than -18 °C is specified for Grade No. 2-GT, the minimum viscosity shall be 1.7 mm<sup>2</sup>/s and the minimum 90% recovered temperature shall be waived.

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The elimination of non-manganese metals from the turbine co-fuels may be desirable, unless contemplated as a ECS metallic component. Although other lower trace amounts of certain metals in gas turbine fuel oils may promote longer turbine service from a corrosion standpoint. However, the imposition of exceedingly low non ECS metallic levels may limit the availability of the fuel or materially increase its cost. Thus, in the practice of this invention metals (unless contemplated as an ECS metallic) should not be included above trace levels. For example, in fuel gas oils No.0-GT to No.3-GT vanadium (except if employed as an ECS metal) should not exceed 0.5 mg/kg, sodium plus potassium (except if employed as an ECS metal) should not exceed 0.5mg/kg, calcium (except if employed as an ECS metal)not exceeding 0.5 mg/kg. It is also preferred the limits of these metals not exceed 0.05 to 0.001 mg/kg. However, Applicant has found the hazards or their inclusion with an ECS fuel to be substantially mitigated.

Lead is not preferred in the practice of this invention, and should be excluded, where possible. However, it may be present in trace concentrations in gas turbine co-fuels due to normal handling in the above fuels so long as it does not exceed 0.5 mg/kg, preferably 0.001 mg/kg.

It is noted that sodium and potassium can combine with vanadium to form eutectics which melt at temperatures as low as 566°C and/or can combine with sulfur in the fuel to yield sulfates with melting points in the operating range of the gas turbine.

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These compounds produce severe corrosion, and for turbines operating at gas inlet temperatures above 650°C additives are not yet in general use which control such corrosion. Accordingly, the sodium-plus-potassium level must be limited, but each element is measured separately.

For gas turbines, operating at turbine inlet gas temperatures below 650°C (1200°F), the corrosion due to sodium compounds is of minor importance and can be further reduced, if necessary, by silicon-base additives, and is a preferred embodiment of this invention.

Sodium may be beneficial in certain turbines applications, because it increases the water-solubility of the deposits and thereby increases the ease with which gas turbines can be water-washed to obtain recovery of the operating performance.

It is contemplated in the practice of this invention that sufficient sodium plus potassium levels, with reduced inlet gas temperatures from ECS containing gas turbine fuels, be employed.

Calcium is not harmful from a corrosion standpoint; in fact, it serves to inhibit the corrosive action of vanadium. However, calcium can lead to hard bonded deposits that are not self-spalling when the gas turbine is shut down, and not readily removed by water washing of the turbine. Due to instant inventions capability to reduce combustion temperatures, calcium deposits are not as problematic. However, calcium concentrations in the fuel should be not be excessive.

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Absent Applicant's combustion and temperature capabilities, vanadium can form compounds such as vanadium pentoxide that melts at 691°C, and causes severe corrosive attack on all of the high temperature alloys used for gas turbine blades. If there is sufficient magnesium in the fuel, it will combine with the vanadium to form compounds with higher melting points and thus help reduce the corrosion rate. Furthermore, ash deposits form in the turbine and may be problematic. Thus, it is a preferred embodiment to reduce combustion temperatures in the practice of Applicant's invention to below 650°C.

It is still advisable, when vanadium is present in more than trace amounts either in excess of 0.5 mg/kg or a level recommended by the turbine manufacturer, to maintain a weight ratio of magnesium to vanadium in the fuel of not less than 3.0 in order to control corrosion.

Even, with turbine inlet gas temperatures of this invention below 650°C, wherein the corrosion of the high-temperature alloys is of minor importance, it is advisable to prophylactically use a silicon-base additive to further reduce the corrosion rate by absorption and dilution of the vanadium compounds.

Thus, it is an express object and a preferred embodiment of instant invention to operate said engines employing ECS fuels, wherein inlet temperatures are reduced to below 650°C or 600°C. It is acceptable to operate said engines, where turbine inlet temperatures are reduced further to below 550°C or even 400°C, if circumstances

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warrant. It is contemplated that these reduced turbine inlet temperatures are achieved when employing Applicant's ECS fuels and/or reducing the end boiling and T-90 fractions, in the manner described herein.

5 It is also expressly contemplated that film cooling (effusion cooling) on turbine blades may be additionally employed, if necessary, to reduce high temperature corrosion.

In the practice of this invention the preferred minimum flash point of Applicant's gas oil turbine fuels is  
10 100°F. In 3-GT and 4-GT fuels the minimum preferred flash point is 130°F. Flash points below 100°F and 130°F are acceptable, but less preferred.

The preferred pour point of Applicant's gas oil fuels is 6°C below the ambient temperature at which the turbine is  
15 operated, except where fuel heating facilities are provided.

Carbon residue is a measure of the carbonaceous material left in a fuel after all the volatile components are vaporized in the absence of air. It is a rough  
20 approximation of the tendency of a fuel to form carbon deposits in the combustor of the gas turbine. Combustion systems designed for use on Grades 3-GT and 4-GT are insensitive to this property, but other gas turbines (including aviation jet turbines) normally require a limit  
25 on the carbon residue. In the practice of this invention, carbon residue found in the 10% distillation residue, as a percentage of mass ash (employing ASTM practices), should generally not exceed 0.15 in No. 0-GT and No. 1-GT fuels,

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and 0.35 in No. 2-GT fuels. However, lower mass concentrations are preferred.

5 With increasing burning velocities and lower combustion temperatures of Applicant's invention, carbon deposits are effectively controlled. Thus, residue mass concentrations in fuels outside those noted above are likely to be acceptable, because their adverse effect will likely be mitigated by Applicant's invention.

10 In the practice of Applicant's invention, the modification of distillation temperatures, as taught herein, is especially contemplated, especially where such practice results is a reduction of end point/T-90, control or reduction of T-50, and/or T-10 distillation fraction temperatures, which in turn improve combustion, reduce free  
15 carbon formation, emissions and/or smoke. Applicant has discovered volatility/distillation modification further reduces the formation of free carbon in the primary combustion zone, especially when in combination with an ECS fuel, such as dimethyl carbonate and an organo-metallic.

20 In the practice of this invention, kinematic viscosity should approximate or exceed viscosity prescribed under ASTM D 2880 specifications.

25 Sulfur, which normally burns to sulfur dioxide, can be partially oxidized to sulfur trioxide, which then can combine with sodium and potassium compounds from the ash in the fuel to form sulfates, pyrosulfates, and such compounds as sodium or potassium iron trisulfate. The pyrosulfates, and the trisulfates have melting points in the operating

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range of the gas turbine. Hence, these compounds produce severe corrosion of the turbine blading.

Historically, it has been found impractical to prevent corrosion by limiting the sulfur content of the fuel, so corrosion of this type is controlled by limiting the sodium and potassium. Gas turbines with waste heat recovery equipment may require additional sulfur control to prevent cold-end corrosion.

However, in the practice of Applicant's invention it is desirable to limit sulfur concentrations to the maximum extent possible. Sulfur concentrations less than 0.4 mass percent are desirable. However, Lower sulfur concentrations of 0.1 mass percent down to 0.05 mass percent, or lower, are more desirable. Those even as low as 0.01 mass percent are also preferred. Fuels absent or essentially absent sulfur are particularly preferred.

However, in the practice of Applicant's invention, which achieves reduced combustion temperatures, sulfur oxidation and related corrosion problems are not as significant, and can be effectively controlled. Thus, higher concentrations of sulfur are permissible, if practical circumstances warrant.

#### Diesel Fuel Oils and Systems

As noted, this invention contemplates a wide range of diesel fuel oils and related system applications. Non-limiting examples of diesel co-fuels and resultant fuels, include fuels meeting ASTM D 975 (incorporated by

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reference), industry, international specifications, and/or EPA specifications, certification standards and/or regulations, present and future, synthetic diesel, bio diesel, etc. See TABLE 3. Non-limiting examples of diesel  
5 fuel engines contemplated in Applicant's invention include: indirect injection, improved indirect injection and advanced ignition assisted diesel engine systems, direct injection, and the like.



TABLE 3

## ASTM D 975

DETAILED REQUIREMENTS FOR DIESEL FUEL OILS<sup>4</sup>

Property	ASTM Test Method <sup>b</sup>	Grade Low		Grade No. 1-D		Grade No. 2-D		Grade No. 1-D <sup>c</sup>		Grade No. 2-D <sup>c</sup>		Grade No. 4-D <sup>c</sup>	
		Sulfur	No. 1-D	Sulfur	No. 1-D	Sulfur	No. 2-D	Sulfur	No. 1-D <sup>c</sup>	Sulfur	No. 2-D <sup>c</sup>	Sulfur	No. 4-D <sup>c</sup>
Flash Point, °C, min.	D93	38	52	38	52	38	52	38	52	38	52	55	55
Water & Sediment, % vol, max.	D1796	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.50	0.50
Distillation Temperature, °C 90% % vol.	D86												
Recovered													
min													
max													
Kinematic Viscosity, mm <sup>2</sup> /S at 40°C	D445												
min													
max													
Ash % mass, max	D482	0.01											
Sulfur, % mass, max <sup>f</sup>	D2622 <sup>f</sup>	0.05											
	D129	...											
	D130	No.3											
Copper strip corrosion rating max 3 h at 50°C													
Cetane number, min <sup>g</sup>	D613	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	40 <sup>h</sup>	30 <sup>h</sup>	30 <sup>h</sup>
One of the following properties must be met:													
(1) Cetane index, min.	D976 <sup>†</sup>	40	40	40	40	40	40	40	40	40	40	...	...
(2) Aromaticity, % vol, max.	D1319 <sup>f</sup>	35	35	35	35	35	35	35	35	35	35	...	...

RECTIFIED SHEET (RULE 91)

TABLE 3  
(continued)  
ASTM D 975  
  
DETAILED REQUIREMENTS FOR DIESEL FUEL OILS<sup>A</sup>

Property	ASTM Test Method <sup>B</sup>	Grade Low		Grade No. 2-D		Grade No. 1-D <sup>C</sup>		Grade No. 2-D <sup>C</sup>		Grade No. 4-D <sup>C</sup>	
		Sulfur No. 1-D	Sulfur No. 2-D								
Cloud point, °C, max.	D2500	†	†	†	†	†	†	†	†	†	†
Ramsbottom carbon residue on 10% distillation residue, % mass, max	D524	0.15	0.35	0.15	0.35	0.15	0.35	0.35	0.35	...	...

<sup>A</sup> To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller and manufacturer.

<sup>B</sup> The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 4.1.

<sup>C</sup> Grades No. 1-D, No. 2-D and No. 4-D are required to contain a sufficient amount of 1,4-dialkyl amino anthraquinone (blue dye) so its presence is visually apparent.

<sup>D</sup> When a cloud point less than -12°C is specified, the minimum flash point shall be 38°C, the minimum viscosity at 40° shall be 1.7 mm<sup>2</sup>/s and the minimum 90% recovered temperature shall be waived.

<sup>E</sup> Other sulfur limits can apply in selected areas in the United States and in other countries.

<sup>F</sup> These test methods are specified in CFR 40 Part 80.

<sup>G</sup> Where cetane number by Test Method D 613 is not available, Test Method D 4737 can be used as an approximation.

<sup>H</sup> Low ambient temperatures as well as engine operation at high altitudes may require the use of fuels with higher cetane ratings.

<sup>I</sup> It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. However, satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6°C above the tenth percentile minimum ambient temperature for the area in which ambient temperatures for U.S. locations are shown in Appendix X2. This guidance is general. Some equipment designs or operation may allow higher or require lower cloud point fuels. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures.

† Editorially corrected.

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It is a further embodiment of this invention that Applicant's fuels include future reformulated diesel fuels of the calibre to be defined either by industry or government.

5           Thus, it is an embodiment to incorporate an ECS fuel and a diesel co-fuel, such that the resultant fuel meets the above specifications, present and future.

          In the practice of this invention, Mn operating ranges in the resultant diesel composition may range from 0.001 to  
10       about 10.00, .001 to 7.0, .001 to 5.0, .001 to 4.0, 0.001 to 3.5 gram Mn/gal. It appears optimum Mn levels are less than 5 gr./gal, with those less than 3.0 or even 2.5 gr. Mn/gal being more desirable. However, concentrations greater than 10, 12, 15, 20, 22, 25, 26, 27, 28, 29, 30,  
15       31, 32, 35, 40, 50 grs Mn/gal are also contemplated. For purposes of improving combustion, a desireable range includes from about 0.001 to about 3.00 gram Mn/gal, Other concentrations include those equal to or greater than 0.015625, 0.03125, 0.0625 0.125, 0.25, 0.275, 0.375, 0.50,  
20       0.625, 0.75, 0.875, 1.0, 1.125, 1.25, 1.375, 1.5, 1.625, 1.874, 2.0, 2.125, 2.25, 2.375, 2.5, 2.625, 2.75, 2.875 gram Mn/gal. A desireable range includes from about 0.001 to about 1.50 gram Mn/gal. Other desireable ranges include from about 0.001 to about 0.50 gram Mn/gal of composition.  
25       Lower concentration ranges from .001 to about 0.25 grams/gal are also contemplated. Ranges greater than 0.0625 gr Mn/gal are also contemplated.

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However, as noted above, the greater the O<sub>2</sub> concentrations contained in the fuel composition, especially with superior ECS compounds, the greater the permissible Mn concentrations. Also with heavier fuel compositions manganese concentrations may be increased. A synergism occurs complimenting the usage of ECS compounds and Mn, particularly when T-90 temperature are reduced. Differing fuel specifications, operating conditions, environmental requirements, and combustion systems will dictate final compositional construction.

Applicant notes the desirable oxygen of his ECS component by weight in diesel compositions, which yields good results normally exceeds at least 1.0% by weight, and those equal to or exceeding 1.5%, 1.75%, 2.0% are desireable. However, in the practice of this invention lower O<sub>2</sub> concentrations are contemplated, including to a low as 0.01 weight percentage.

In the practice of this invention oxygen concentrations ranging from 0.01 to 0.5% weight is acceptable. Oxygen concentrations from 0.01 to 1.5% weight percent is desireable. O<sub>2</sub> concentrations from about 0.5 to 5.0%, and those greater than 1.5% slightly more preferred. Acceptable oxygen ranges, when the ECS fuel constitutes a significant minority or greater percentage of the composition includes oxygen weight concentrations of 5.0%, 10%, 15%, or 20%, or greater. In larger diesel fuel engines, including locomotive, marine and large stationary industrial applications, it is anticipated that the fuel

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compositions will contain O<sub>2</sub> concentrations of 2% weight, or more. There are no maximum limits anticipated in advanced applications. Hence, in the practice of this invention, O<sub>2</sub> concentrations maximizing the advantages of Applicant's invention are expressly contemplated.

Applicant has unexpectedly discovered that diesel emissions, including particulates, HC, CO and NO<sub>x</sub> emissions are materially reduced in the practice of Applicant's invention. Such reductions appear to be closely tied to the invention's increases in burning velocities and reductions in combustion temperatures. Applicant has also unexpectedly discovered that due to increases in burning velocities and lower combustion temperatures that diesel engine noise can be controlled, without sacrificing economy and emissions.

The properties of commercial distillate diesel fuels depend on the refinery practices employed and the nature of the crude oils from which they are derived. Thus, they may differ both with and within the region in which they are manufactured. Such fuels generally boil over a range between 163 and 371°C (325-700°F). Their makeup can represent various combinations of volatility, ignition quality, viscosity, sulfur level, gravity, and other characteristics. As noted, the fuels included in Applicant's invention include:

Grade low sulfur No. 1-D, which is a special purpose, light distillate fuel for automotive diesel engines requiring low sulfur fuel and requiring higher volatility

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than that provided for Grade low sulfur No 2-D, and is met to comply with 40 CFR Part 80 regulations.

Grade Low Sulfur No. 2-D, which is a general purpose middle distillate fuel for automotive diesel engines requiring low sulfur fuels. It is also suitable for use in non-automotive applications, especially in conditions of varying speed and load. This grade is also in conformity with 40 CFR Part 80 regulations.

Grades No. 1-D and No. 2-D, which are similar in purpose to their low sulfur counter parts, except that their sulfur contents are not as strictly regulated.

Grade No. 4-D, which is a heavy distillate fuel, or a blend of distillate and residual oil, for low and medium speed diesel engines in non-automotive applications involving predominately constant speed and load.

Type C-B - Diesel fuel oils for city-bus and similar operations

Type T-T - Fuels for diesel engines in trucks, tractors, and similar service

Type R-R - Fuels for railroad diesel engines

Type S-M - Heavy-distillate and residual fuels for large stationary and marine diesel engines.

It is anticipated the hydrocarbon composition of Applicant's diesel fuels will be tailored to maximize the beneficial aspects of ignition quality, heating value, volatility, gravity, oxidation stability, etc., to positively effect power, economy, wear, deposit formation,

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starting, and smoke performance of applicants diesel engines.

5 Since diesel fuels are complex mixtures of many individual hydrocarbons, it is also important in the practice of this invention, to construct the diesel fuel to maximize the increased burning velocity and/or reduced combustion temperature objects of Applicant's invention.

10 It is noted that the practice of employing an ECS based diesel fuel normally improves ignition quality, which in turn positively influences cold starting, warmup, combustion roughness, acceleration, deposit formation under idle and light load operation, and exhaust smoke density. The ignition quality requirement of an engine depends on design, size, mechanical condition, operating conditions, 15 atmospheric temperature, and altitude. However, increased ignition quality over the level required does not materially improve engine performance.

In the practice of this invention a cetane number of 30 is desireable. A cetane number of 40 or greater is 20 preferred, especially in low sulfur No. 1-D and low sulfur No. 2-D fuels. An optimal cetane number in the practice of this invention is greater than 48. However, cetane numbers greater 60 or 70 are also preferred.

25 It is also a preferred practice, when employing low sulfur diesel fuels Grade No. D-1 and No. D-2 to have a minimum cetane index number, a limitation on the amount of high aromatic components, of 40 (as measured by ASTM D 976) or an aromatic content not exceeding 35% by volume (as

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measure by ASTM D 1319). Lower aromatic contents, as previously noted, are more preferred. Especially those not exceeding 30% by volume, with those less than 20% more preferred, and those less than 10% most preferred.

5           However, it is important that cetane not be excessively increased, with use of ignition or cetane improves, which may act to increase particulate emissions independent of injection timing. Ignition quality is measured by ASTM D 613, Test Method for Ignition Quality of  
10 Diesel Fuels by the Cetane Method.

#### Example 84

A composition comprising an a combustion improving amount of an ECS fuel (preferably containing diethylene glycol dimethyl ether or diethylene glycol dimethyl ether),  
15 and a combustion improving amount of a cyclopentadienyl manganese tricarbonyl compound, and a diesel fuel base.

#### Example 85

20           The composition of example 84, alternatively containing a combustion improving amount of methylene dimethyl ether.

#### Example 86

25           The composition of example 84, alternatively containing a combustion improving amount of dimethyl ether.



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Example 87

In combination, a diesel fuel meeting ASTM 975 specifications and a diesel combustion system; said combination being characterized in that: said fuel contains  
5 a combustion improving amount of dimethyl carbonate and/or methylene di methyl ether, and a cyclopentadienyl manganese tricarbonyl compound having a concentration ranging from about 0.001 to about 2.5 gr Mn per gallon; whereby  
10 resultant fuel combustion results in improved thermal efficiency and/or fuel economy.

Example 88

A No. 2 diesel fuel composition comprising a minor portion of a combustion improving amount of dimethyl  
15 carbonate and a cyclomatic manganese tricarbonyl, and a major portion of a base diesel fuel, such that resultant fuel has a cetane of 42 to 50 (preferably substantially greater), an aromatic content of less than 28 volume  
percent (preferably less than 20%, more preferably 15%,  
20 most preferably less than 10%), a T-90 temperature of 560°F to 600°F (more preferably less than 540°F, 520°F, 500°F or lower), a sulfur content of 0.08 to 0.12% mass (more  
preferably 0.05% or sulfur free), an API gravity of 32 to  
37 (more preferably higher), and a minimum flash point of  
25 130°F.

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Example 89

A No. 1 diesel fuel composition containing a minor portion of a combustion improving amount of dimethyl carbonate and a cyclomatic manganese tricarbonyl, and a major portion of a base diesel fuel, such that resultant fuel has a cetane of 48 to 54 (preferably substantially greater), aromatics representing 10% or less by volume, a T-90 temperature of 460°F to 520°F (more preferably less than 425°F, or lower), a sulfur content of 0.08 to 0.12% mass (more preferably less than 0.05% mass), API gravity of 40 to 44 (more preferably higher), and a minimum flash point of 120°F.

Example 90

The examples of 88-89, wherein fuel meets ASTM D 975 specifications.

Example 91

A method for operating a diesel engine, said method comprising injecting the fuels of examples of 88-90 (including a substituted No. 5-heavy) by means of high pressure direct fuel injection system, employing pressures ranging from 30 MPa to 120 MPa, wherein the average vapor particle size is less than 70 microns, more preferably 40-60 microns; whereby burning velocity is increased.

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Example 92

The examples of 80-91, wherein the combustion system additionally comprises a turbocharger, an ERG system, and wherein the fuel injection system employs sensor input means to regulate fuel injection rate and/or timing.

Example 93

The examples of 80-92, wherein resultant exhaust emissions meet U.S. EPA and Clean Air Act regulations, including 42 USC 7545 et seq.

In the practice of this invention ignition promoters may be employed, individually and/or in combination with ECS compounds, particularly in fuels which require higher temperatures to ignite, which extends their period of ignition. Such promoters include di-tertiary butyl peroxide, alkyl peroxides, alkyl hydroperoxides, alkyl nitrate additives, including ethyl-hexyl nitrate and isopropyl nitrate, 2,5 dimethyl 2,5 di(tertiary butyl peroxy) hexane, tertiary butylcumyl peroxide, di(tertiaryamyl) peroxide, tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, and mixtures thereof.

In the diesel practice of this invention, it is preferred that aromatic concentrations and T-90 temperatures be reduced when ever possible.

In the practice of Applicant's invention, it is desireable that a combination of high mixing rate and long ignition delays be incorporated with premixed, homogeneous ECS containing fuels, when ever possible. However, such

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practice should not be in the extreme so as to cause structural problems, due to increased cylinder pressures.

This invention also contemplates certain engine modifications, including combustion chamber modified designs, fuel injection timing and characteristics noted  
5 above, blowing or turbocharging, especially in combination with direct injection engines, and use of exhaust gas recirculation and exhaust gas after treatment systems, including traps, trap-oxidizers, regenerative trap-oxidizers, and catalysts.  
10

#### Example 94

A low emission No. 2 grade diesel fuel comprising a minimum cetane number of 52, maximum fuel sulfur of 350 ppm  
15 (more preferred less than 0.05% mass), aromatics less than 30% volume (more preferably less than 15%), a combustion improving amount of dimethyl carbonate and a combustion improving amount of a cyclomatic manganese tricarbonyl compound.

20

#### Example 95

A low emission diesel fuel comprising a minimum cetane number of 52, maximum fuel sulfur less than 100 ppm, aromatic content of 12%, T-90 temperature of 475°F, bromine  
25 number of 0.10, a combustion improving amount of dimethyl carbonate ranging from 0.5 to 4.0% oxygen by weight, and a combustion improving amount of a cyclomatic manganese tricarbonyl compound.

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Example 96

The fuel composition of 94-95, wherein the aniline point less than 145°F.

5      Example 97

A low emission diesel fuel comprising a minimum cetane number of 62, maximum fuel sulfur less than 0.01% weight, 10% aromatic content, olefin 41% by weight (preferred less than 10%), T-90 temperature of 514°F, bromine number of 10      0.10, aniline point less than 145°F, a combustion improving amount of dimethyl carbonate and/or diethylene glycol dimethyl ether (or diethylene glycol diethyl ether), and a combustion improving amount of a cyclomatic manganese tricarbonyl compound.

15

Example 98

The composition of Example 97, wherein said composition is combusted in a heavy duty truck engine and HC, CO, NOx, and particulate emissions are 1.3, 15.5, 4.0, 20      0.10 gm/bhp-hr, respectively.

In the practice of Applicant's invention, his diesel fuels contain sufficient heating value to efficiently operate the diesel engine at improved thermal efficiencies. The fuel's gravity/density, along with its volatility, 25      provides useful information about the composition of the fuel, which in turn relates to its heating value, power and economy, deposition, wear, and exhaust smoke.

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Generally, the power and economy of diesel engines are insensitive to volatility directly, although the less volatile fuels of Applicant's invention normally will have a higher heating value and thus indirectly affect these performance factors. On the other hand, starting and warm up are favored by high front end volatility, and deposition, wear, and exhaust smoke in some engines are increased by high 90% and end points.

Thus, in the practice of Applicant's invention volatility modification of diesel fuels, reducing end point, T-90, T-50, T-10 temperatures and the like, is expressly contemplated in order to improve combustion efficiency and/or reduce hazardous emissions. Reductions in end point and T-90 temperatures being most preferred.

It is an embodiment of this invention that the emissions of Applicant's fuels, including diesel fuels, meet ASTM, CAA requirements and/or other governmental regulations, current and future.

Diesel fuel viscosity can affect the performance of fuel systems. Low viscosity can result in excessive wear in some injection pumps and power loss due to pump and injector leakage. High viscosity can result in excessive pump resistance or filter damage. Fuel spray characteristics are also influenced by viscosity. Thus, in the practice of this invention kinetic viscosity measured in  $\text{mm}^2/\text{S}$  at  $40^\circ\text{C}$  should have minimum values of 1.3, 1.9, 1.3, 1.9, 5.5 for diesel grades low sulfur No. 1-D, low sulfur No. 2-D, No. 1-D, No. 2-D, and No. 4-D,

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respectfully. The maximum values should not exceed 2.4, 4.1, 2.4, 4.1, 24.0 for diesel grades low sulfur No. 1-D, low sulfur No. 2-D, No. 1-D, No. 2-D, and No. 4-D, respectively. However, it is expressly contemplated that  
5 viscosities outside these ranges are acceptable in the practice of this invention, especially in conjunction with the disclosed ECS compounds/fuels and/or mechanical means of this invention.

10 In the practice of this invention fuels which do not contain a pour point depressant additive, the pour point is usually from 3°C (5°F) to 15°C (25°F) below the cloud point.

In the practice of this invention a minimum flash point of 38°C for Grades No. 1-D, and 52°C for Grades 2-D and 4-D are preferred. However, in the practice of this  
15 invention flash points outside these temperatures are contemplated.

In the practice of the instant invention sulphur content of 500 parts per million is acceptable, however concentrations lower are more preferred. Most preferred  
20 concentrations are those of 50 parts per million or less. Sulfur weight percentage of 0.05% or less are also preferred. Sulfur concentrations of 0.05% mass or less is required in Grade low sulfur 1-D and 2-D.

25 In the practice of this invention, carbon residue found in the 10% distillation residue, as a percentage of mass, should generally not exceed 0.15 in No. 1-D fuels, and 0.35 in No. 2-d fuels. However, lower mass concentrations are more preferred. In the practice of

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this invention the maximum percent of ash by mass, using ASTM D 482, is 0.01%, except for Grade No. 4-D, which is 0.10%. Lower ash percentages are preferred. However, the lower combustion temperatures of Applicant's invention tends to mitigate ash related problems.

In the practice of this invention the ASTM Copper Strip Tarnish Test should have a maximum rating of No. 3.

It is an embodiment of this invention that diesel fuels be anhydrous or essentially anhydrous, except in separate fuel/ECS/water injection or emulsions circumstances.

It is also preferred that Applicant's diesel fuels have reduced products of oxidation, resulting from storage, which in turn can cause the formation of deposits, filter plugging, and lacquering of fuel pump and injector parts.

In the practice of this invention, additives are



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contemplated including ignition quality improver, oxidation inhibitors, biocides, rust preventives, metal deactivators, pour point depressants, demulsifiers, smoke suppressants, detergent-dispersants, conductivity improver, dyes, de-  
5 icers and additives to reduce and/or control fuel injector deposits.

For example, the high molecular weight polyisobutylene substituted amine derivative TFA-4681, a Texaco detergent/  
dispersant is contemplated. Additional  
10 detergent/dispersants, include fuel soluble salts, amides, imides, oxazolines and esters of long aliphatic hydrocarbon-substituted dicarboxylic acids or their anhydrides, long chain aliphatic hydrocarbons having a polyamine attached directly thereto, a Mannich condensation  
15 product(s) formed by condensing a long chain aliphatic hydrocarbon-substituted phenol with an aldehyde, preferably formaldehyde, or similar additive is contemplated in the practice of keeping fuel injectors and valve intakes clean.

20 Smoke suppressants, including organic compounds of barium, particularly the barium carbonate overbased barium sulfonates, N-sulfinyl anilines, are contemplated, as well as others.

Additional deposit control additives include, a  
25 polyether amine sold by Oronite Chemical as OGA-480, a polyalkenyl succinimide sold by Ethyl Corp as HITEC 4450, a polyisobutenyl amine sold by Oronite Chemical as OGA-472, and the like.

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Example diesel fuel additives are shown by class and function in Table 4. As with any system in which a variety of additives may be used, care should be taken to avoid incompatibilities among additives and unanticipated interactions which may produce undesirable fuel effects.

5

TABLE 4

## COMMERCIAL DIESEL FUEL ADDITIVES - FUNCTION AND TYPE

5	Class or Function	Common Additive Type
10	1. Ignition quality Improver - Raise Cetane Number thereby promoting faster starts and less white smoke.	Alkyl nitrates.
15	2. Oxidation Inhibitors - Minimize oxidation and gum and precipitate formation, improve storage life.	Alkyl amines and amine-containing complex materials.
20	3. Biocides - Inhibit the growth of bacteria and fungi which feed on hydrocarbons, help prevent filter-clogging caused by these organisms.	Boron compounds, ethers of ethylene glycol, quaternary amine compounds.
25	4. Rust Preventives - Minimize rust formation in fuels systems and storage facilities.	Organic acids and amine salts. A widely-used type is based on dimerized linoleic acid.
30	5. Metal Deactivator - Deactivates copper ions which are powerful oxidation catalysts.	N,N'-disalicylidene-1,2-propane diamine.
35	6. Pour Point Depressants - Reduce the pour point and improve low-temperature fluidity properties by modifying the wax crystal growth, structure, and/or agglomeration.	Generally consist of polymeric materials such as polyolefins, polyacrylates, polymethacrylates, modified polystyrenes, ethylene-vinyl acetate copolymers, and ethylene-vinyl chloride copolymers.

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- |    |     |   |  |
|----|-----|---|--|
|    | 7.  | Demulsifiers and Dehazers - improve the separation of water from distillate fuels and prevent haze.   | Surface-active materials which increase the rate of water/oil separation. Usually quite complex mixtures.  |
| 5  | 8.  | Smoke Suppressants - Minimize exhaust smoke by catalyzing more complete combustion of carbonaceous materials or by helping to maintain fuel spray patterns.   | Catalyst types are generally overbased barium compounds. Maintenance of spray patterns is helped by detergents.                                    |
| 10 | 9.  | Detergent-Dispersants - Promote engine fuel system cleanliness, help prevent nozzle deposit formation and injector sticking, interfere with precipitate agglomeration, thus maintaining optimum filtration characteristics. | These are usually surface-active agents. They are often polymeric materials containing amines and other functional groups.                         |
| 15 |     |   |  |
|    | 10. | Conductivity Improver - Improve dissipation of electrostatic charge.  | Amine salts, metallic salts, and polymeric compounds.  |
| 20 |     |   |  |
|    | 11. | Dyes - Various identification purposes including tax status.  | Oil-soluble solid and liquid dyes.   |
| 25 | 12. | De-icers - Reduce the freezing point of small amounts of water to prevent fuel line plugging.   | Low molecular weight alcohols (ethanol, isopropanol, and/or methanol), and ethylene glycol monomethyl ether or diethylene glycol monomethyl ether. |
| 30 |     |   |  |
|    |     | Note: Some materials may also be marketed as multifunctional or multipurpose additives, performing more than one of the functions.  |  |

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In the practice of this invention the use Grade No. 2-D or its low sulfur equivalent at ambient temperatures above  $-7^{\circ}\text{C}$  ( $+20^{\circ}\text{F}$ ) is recommended. At very low temperatures, the use of No. 1-D fuel or its low sulfur equivalent is recommended, which usually forms fewer wax crystals and thus has much lower cloud and pour points.

In the practice of this invention winterized or climatized No. 2-D fuel is also recommended. Such fuels can be made by diluting No. 2-D with No. 1-D or kerosene to lower the cloud and pour points as required. It is preferred that the cloud point (or wax appearance point) be  $6^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ) above the tenth percentile minimum ambient temperature for the area in which the fuel will be used.

In the practice of this invention pour point depressants, flow improver, or wax modifiers, can be used to change the size and/or shape of wax crystals, and thus minimize cold weather problems. The additive type and concentration must be optimize for a specific fuel, and the additive must be thoroughly blended into the fuel at temperatures well above the cloud point. Therefore, such additives are most effective when blended by fuel suppliers rather than by equipment users. These additives will not lower the cloud point, but they can lower the temperature at which fuel filter plugging due to wax crystals occurs.

The fuel properties most often associated with effects on exhaust emissions are aromatic content, volatility, gravity, viscosity, cetane number, and the presence of specific elements (for example, hydrogen and sulfur).

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Increased aromatic content generates increased particulate (especially soluble organic particulate) and hydrocarbon emissions.

5 However, the application of Applicant's invention, increasing burning velocity and/or reducing combustion temperatures, with CMT, greatly mitigates the problematic nature of most of the fuel properties associated with aggravating emissions, including aromatics in diesels, which in Applicant's opinion may be overstated. See for  
10 example, "Effects of Fuel Properties on Diesel Engine Emissions--A Review of Information Available to the EEC-MVEG Group," SAE Paper 910608, 3/1/91.

In the practice of this invention, the mitigation of diesel hydrocarbon emissions is a particularly object, as  
15 Applicant does not believe those in the art are fully aware of the photochemical reactivity of diesel HC emissions.

Higher distillation temperatures of the lower-vapor-pressure components (for example, T-50 and T-90 points) generally result in higher particulate emissions, although,  
20 for typical variations in aromatics and volatility, the volatility effect is often small. Fuel gravity, viscosity, cetane number, and hydrogen content usually correlate with volatility and aromatic content.

In the practice of Applicant's invention it has been  
25 found that it is desireable to keep the local carbon/oxygen ratio below 0.5, as an effective means of additionally controlling particulate emissions.

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In the practice of this invention it is contemplated that advanced lubricating oils and technologies as an additional means for reducing particulate emissions.

5 It is the art belief that NOx and CO emissions are unaffected by modifications to fuel properties. However, as disclosed above Applicant's invention, due to it improved burning velocities and reduced combustion temperatures, unexpectedly reduces both NOx and CO emissions. This is another substantial departure from the  
10 prior art.

#### EXAMPLE TESTS

In order to illustrate the attributes and objects of this invention, Applicant conducted a series of gasoline  
15 fuel tests. (Applicant notes that these example tests were conducted in a spark-ignited internal combustion engine, but the principal elements of the invention, namely those leading to improvements in combustion burning velocity and temperature reductions, are translatable to all Applicant's  
20 contemplated combustion systems, as will be seen below.)

#### EXAMPLE TEST FUELS

A. MEOH FUEL 0.033025 grams manganese of MMT  
per liter of composition, 5% methanol and 5% ethanol by  
25 volume, and unleaded gasoline base.

B. ISO/HEX FUEL 0.033025 grams manganese of MMT  
per liter, 10% isopropanol and 10% hexanol by volume, and  
unleaded gasoline base.

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C. MTBE FUEL 0.033025 grams manganese of MMT per liter, 14.6% MTBE by volume, and unleaded gasoline base.

D. DMC FUEL 0.033025 grams manganese of MMT per liter, 4.6% Dimethyl Carbonate (DMC) by volume, and  
5 unleaded gasoline base.

E. METHYLAL FUEL 0.033025 grams manganese of MMT per liter, 7.2% Methylal by volume, and unleaded gasoline base.



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F. THF FUEL 0.033025 grams manganese of MMT per liter, 1.6% Tetrahydrofuran by volume, and unleaded gasoline base.

5 G. HIGH MANGANESE (Mn) FUEL 0.5284 grams manganese of MMT per liter, 5% Methanol by volume, and unleaded gasoline base.

H. MANGANESE FUEL 0.033025 grams manganese of MMT per liter, and unleaded gasoline base.

10 I. BASE FUEL Unleaded gasoline base (clear fuel).

#### Test Methodology

15 The above example fuels were tested in a 1988 Chevrolet C1500 pickup truck with a 350 CID V-8 engine, having a throttle-body fuel injection system and oxygen sensor-closed loop fuel control. The inclusion of this oxygen sensing system provided a means of adjusting the stoichiometry to compensate for variations in the oxygen content of the various test fuels. This feature eliminated bias in HC and NOx emissions due to oxygen content differences. In other words, a test fuel with a high oxygen content, tending to enlean combustion, would not necessarily show better or worse emissions than the fuel containing little or no oxygen.

25 The engine heads and valves were cleaned before each fuel was tested. A new oxygen sensor and new spark plugs were also installed.

Each fuel was subjected to two (2) principal tests. The First Test ("Test One") measured HC and NOx emissions

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from the engine over a forty (40) hour, steady state, 1000 rpm, no load cycle. The purpose of this no load, steady state test was to elicit worse case hydrocarbon (HC) emissions over time, e.g. generation of manganese oxides.

5 It is known in the art that low load, idle conditions, are excellent conditions to exacerbate oxide formation, but it translates into HC emission increases as a function of time. Thus, this accelerated test Mn oxide formation and consequently HC emission degradation.

10 Prior to introducing each new test fuel, the clean engine was cured on the BASE fuel ("clear fuel") until exhaust emissions stabilized. This generally required approximately 3 to 6 hours of steady state operation. Hydrocarbon and NOx emissions were measured periodically  
15 utilizing Beckman exhaust emission analyzers. Table 5 sets forth a summary of the test results.

The Second Test ("Test Two") was conducted immediately after the First Test using the same fuel with the same engine still warm. The Second Test was conducted with the  
20 vehicle on a stationary chassis dynamometer. Test measurements were made at 50 mph (80.5 kilometers per hour "kph") under varying load conditions, e.g. from 15 to 24 indicated horse power ("ihp"). This test measured differences in combustion temperatures, fuel economy, HC  
25 and NOx emissions. The test was designed to show improvements of thermal efficiency, which would have been translated into improved fuel economy and emissions. See Figures 1 through 6 for a summary of results.

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**Analysis of TABLE 5**

TABLE 5 sets forth the HC emission results of Test One. TABLE 5 shows moderate HC increases in the clear fuel. This is indicative of the normal deposition of hydrocarbons on cylinder walls, etc., due to low load idle conditions of test 1. The base fuel results provides a bench mark to compare the other fuels. Increases in HC emissions above bench mark would be attributable to manganese oxide coating in manganese fuels.

Table 5 shows all manganese fuels, except Applicant's ECS fuels, to have higher HC increases and/or higher total later stage HC amounts than clear base fuel. Highest increase was in HIGH MN fuel.

In contrast, the ISO/HEX, MECH, MTBE, METHYLAL, and DMC fuels did not show the high HC emission levels of the Manganese fuel (3390 ppmc) (Column D). Their HC emission levels, instead, were materially lower ranging from 2953 to 2024 ppmc for MECH and ISO/HEX, respectively (Column D). Astonishingly, the ISO/HEX, MECH, MTBE, METHYLAL, and DMC hydrocarbon emissions (Column D) are all also below the Base (clear) fuel (3076 ppmc).

Thus, Table 5 shows the increases in HC emissions (and in fact two decreases) for ECS fuels to be significantly lower. In other words, the ECS fuels had better HC emissions than the base fuel. This is accounted for in their improved thermal and combustion efficiencies.

Applicant notes that his ECS fuels ETHYLAL, and DMC actually showed HC emission reductions through out the

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entire test. Meaning that over time, HC emissions actually improved. This is quite an unusual result in any set of circumstances.

5       Applicant notes that the HC emission changes of the last 20 hours of the test (column B) are fairly indicative of expected oxide deposition for Mn fuels. The Manganese, High Mn, and THF fuels all showed materially higher later stage (Column D) HC emissions (3390, 6554, and 4130 ppmc, respectively), than the Base fuel (3067 ppmc).

10       In summary, the Manganese, THF, High Manganese test fuels demonstrate oxide deposition and show considerably high increases in HC emissions over time. In contrast, Applicant's ESC fuels do not show such increases, indicative of no manganese oxide deposition.

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TABLE 5

SUMMARY OF TEST ONE RESULTS

MANGANESE DEPOSITION PHENOMENA  
HYDROCARBON EMISSION INCREASES IN THE PRESENCE OF MN OVER  
TIME

5	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	<u>FUEL</u>	<u>HC CHANGE</u>	<u>TOTAL HC</u>	<u>AVE</u> <u>LATER</u>
	<u>STAGE</u>	<u>LAST 20 HRS (1)</u>	<u>CHANGE (2)</u>	<u>HC ppm (3)</u>
10	Base	38%	45%	3076 (15 HRS)
15	Manganese	41%	31%	3390 (16 hrs)
20	THF hours)	41%	55%	4130 (14
25	High/MN hrs)	31%	1310%	6554 (12.5
30	ISO/HEX	15%	10%	2024 (16 hrs)
35	MEOH	15%	24%	2953 (16 hrs)
	MTBE	4%	17%	2400 (16 hrs)
	Methylal	(9%)	(15%)	2600 (16 hrs)
40	DMC	(25%)	(16%)	2417 (16 hrs)

## NOTES:

45 (1) This column represents the % change of HC emissions of the last half of Test One.

(2) This column represents the total % change of HC emissions over the entire test.

50 (3) This represents the average of the more stabilized, later stage HC emissions. Average calculated for the final hours of the test, as indicated.

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## DESCRIPTION OF TEST TWO "FIGURES 1 THROUGH 6"

## FIGURE 1

Combustion Temperature Differences. This Figure compares engine exhaust gas temperatures ("EGT") of the MANGANESE, BASE, MEOH, MTBE, METHYLAL, and DMC fuels as a function of engine load. Test Two placed the engine under load conditions at 50 mph in order to elicit differences in fuel combustion temperatures, measured by engine exhaust gas temperatures ("EGT").

At 15 ihp the BASE and Manganese fuels are the same at 707°F (375C), while the DMC, MEOH, and METHYLAL fuels range tightly from 717°F (381C), 722°F (383C), and 724°F (384C), respectively. The MTBE fuel, which was tested at 16 ihp, measured 749°F (398C). Thus, the BASE and Manganese fuel have lower exhaust gas temperatures at 15 ihp ranging from 10°F for DMC, 17°F for METHYLAL, to 34°F for MTBE (projected). At loads of over 15.5 ihp the MEOH, DMC, METHYLAL have lower temperatures compared to Base and Manganese fuel. At loads over approximately 16.5 ihp the MTBE fuel has lower temperatures. Thus, at moderate to lower loads BASE and Manganese fuels clearly have lower temperatures.

As load was increased above 15.0 ihp, temperatures increased rapidly for the Manganese and BASE fuels. The Manganese fuel increased the greatest. For example, at 20 ihp, the BASE fuel temperature was 828°F (442C) and Manganese's projected temperature at the same ihp was 860°F (460C).

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In contrast, the MEOH, MTBE, METHYLAL, and DMC fuels had lower rates of EGT increase. For example, at 24 ihp, the MEOH, METHYLAL, and DMC fuels were tightly grouped at 785°F (418C), 795°F (424C), and 798°F (426C), respectively. Similarly, MTBE showed an even lower rate of increase of 778°F (414C) at 22 ihp.

The most significant aspect of Figure 1, is the strong showing that MEOH, MTBE, METHYLAL, and DMC fuels, enjoy markedly lower temperature increases compared to the BASE or Manganese fuels, after reaching a threshold load of 15.5 to 16.5 ihp. For example, Figure 1 shows that at 20 ihp the EGT for the Manganese fuel is 104°F (40C) higher than the MEOH fuel. Additionally, Figure 1 shows that the fuels containing both Mn and an oxygenate (i.e., the MEOH, MTBE, METHYLAL, and DMC fuels) also had significantly lower combustion temperatures than the BASE fuel. For example, the MEOH fuel was 72°F (22C) lower than the BASE fuel.

Figure 1 shows that the higher the load, the greater the EGT differences between the two classes of fuels. Figure 1 indicates that under load conditions oxygenated ECS based fuels unexpectedly reduce combustion temperatures.

## FIGURE 2

**Combustion Temperatures and Hydrocarbon Emissions.** This Figure shows hydrocarbon emissions of Test Two as a function of engine gas temperatures ("EGT"). This Figure shows that there is a direct correlation between HC

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emissions and engine gas temperatures. The relationship is most notable in the MEOH, MTBE, METHYLAL, and DMC fuels. Figure 2 shows that the HC/EGT rate of change for the various oxygenates is higher than the HC/EGT rate of change for the non-oxygenated fuels. Figure 2 shows that the lower the combustion temperature of a given oxygenate, the lower the HC emissions.

Figure 2 is noteworthy because it shows the sensitivity of all the fuels to changes in hydrocarbon emissions to changes in combustion temperatures. It is noted that the BASE and Manganese fuels are not quite as sensitive as the oxygenated ECS based fuels.

### FIGURE 3

**Combustion Temperatures and NOx Emissions.** This Figure shows NOx emission results as a function of EGT. Figure 3, like Figure 2, shows a direct and significant relationship between NOx emissions and EGT for MEOH, MTBE, METHYLAL, and DMC fuels. This Figure clearly shows that at lower EGT's, particularly in the case of the MEOH, MTBE, METHYLAL, and DMC fuels, NOx emissions are much lower than when compared to the BASE and Manganese fuels.

Figure 3 is also noteworthy because it shows the sensitivity of the oxygenated ECS based fuels to changes in NOx emissions as a function to the change of combustion temperatures. It is noted that the BASE and Manganese fuels are again, as in the case of HC's, not sensitive. But, the oxygenated ECS based fuels, showing reduced



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combustion temperatures, unexpectedly show reduced NOx emissions.

**FIGURE 4**

5           **Indicated Burning Velocity.** This Figure measures  
burning velocity indirectly via fuel economy measurements.  
It is known in the art that increases in fuel economy,  
absent a BTU boost, are an indirect indicator of possible  
flame speed changes. Figure 4 shows fuel economy in miles  
10 per gallon ("mpg") (or 0.42566 kilometers per liter "kpl")  
as a function of load (ihp). Figure 4 shows significant  
fuel economy ("FE") differences between the BASE and the  
oxygenated fuels under varying load conditions. On moderate  
loads less than approximately 12.5 ihp (projected) for  
15 MTBE, 14.5 ihp for DMC, and 16.0 ihp for MEOH/METHYLAL,  
base fuel shows superior fuel economy. However, on loads  
greater than approximately 13.0 to 16.0 ihp, fuel economy  
for MTBE, DMC, METHYLAL, MEOH fuels is unexpectedly  
increased.

20           Similar to the exhaust gas temperatures differences  
found in Fig. 1, once a threshold load had been passed,  
fuel economy is markedly improved for ECS fuels. Note,  
that at 20 ihp the fuel economy of the Base fuel is 13.2  
mph (5.619 kpl), compared to 15.7 mpg (6.683 kpl, 15.9 mpg  
25 (6.768 kpl), 16.5 mpg (7.0234 kpl) and 17.2 mpg (7.321 kpl)  
for METHYLAL, MEOH, DMC, and MTBE, respectively.

These material differences account for a 19% to 30%  
improvement in fuel economy over the BASE fuel, under

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moderate to moderately high loads. Thus, the oxygenated ECS based fuels containing METHYLAL, MEOH, DMC, and MTBE show substantial and unexpected fuel economy improvements under loads greater than approximately 15 ihp.

5

**FIGURE 5**

**Burning Velocity and HC Emissions.** This Figure shows HC emissions as a function of fuel economy, i.e. indicated burning velocity. Figure 4 shows a strong correlation between increased burning velocity to improvements in HC emissions. Figure 5 clearly shows that increased burning velocity for METHYLAL, MEOH, DMC, and MTBE translates into improved HC emissions. This correlation is most apparent for the MEOH fuel.

Figure 5 is noteworthy because it shows the sensitivity of the oxygenated ECS base fuels to changes in hydrocarbon emissions as a function to changes in burning velocity. It is noted that all fuels indicate a positive correlation to improvements in HC's as a function of increased burning velocity. However, the base fuel is slightly less sensitive to HC improvement. Methanol appears to have the highest degree of sensitivity. Thus, again the correlations to increased burning velocities with the ECS based fuels, translates into improvements in HC emissions.

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**FIGURE 6**

**Burning Velocity and NOx Emissions.** This Figure shows NOx emissions as a function of fuel economy. This Figure shows a very strong correlation between increased indicated  
5 burning velocity to improvements in NOx emissions. This correlation exists for oxygenated fuels, but is not noticeable for the BASE fuel.

Figure 6 is particularly noteworthy because it shows the sensitivity of the oxygenated ECS fuels to changes in  
10 NOx emissions as a function to changes in burning velocity. It is noted that all fuels indicate a positive correlation to improvements in NOx's as a function of increased burning velocity, except the base fuel, which appears to be unchanged. The sensitivities of the ECS oxygenated fuels  
15 appear to be very high, with methanol again having a slightly higher degree of sensitivity than the others.

**SUMMARY OF FIGURE 1-6**

The figures clearly show that reductions in combustion  
20 temperature operate to reduce emissions. The figures show that the combined reduction in combustion temperatures and increases in burning velocities control adverse emissions. The figures show that after reaching a threshold load of approximately 15 ihp the benefits of Applicant's invention  
25 are most profound.

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**FIGURE 7**

Figure 7 shows different distillation curves due to inclusion of MTBE/oxygenates and modification of mid-range and end-range fractions to improve combustion of MTBE/Mn fuels. Fig. 7 shows a middle distillation region (known as "Technical Enleanment Region") of an MTBE/oxygen fuel with impaired warm driveability. It shows a corrected mid range to avoid impair driveability, and end region for fuel containing MMT at 1/32 gr mn, wherein T-90 temperatures are reduced.

Figure 7 shows optimal T-10, T-90 and T-50 distillation temperature for 1.5% to 2.7% O2 weight of DMC and MTBE fuels containing 1/32 gr. Mn/gal of MMT, which do not debilitate OBD II catalyst monitors. Fig. 7 shows that DMC generally has a much broader range of T-10, T-50, and T-90 temperatures. For example, DMC's T-90 upper range is 410°F, while MTBE's T-90 upper range is generally less than 275°F.

T-50's are equally broad for DMC compared to MTBE, DMC's T-50's range is from 250°F to 150°F, while MTBE's range is from 200°F to 180°F. T-10's show no lower limit for DMC, but MTBE at 80°F.

**GASOLINE COMPOSITIONS**

Automotive gasolines contemplated in Applicant's invention include conventional unleaded, reformulated unleaded, low RVP fuels, and the like. Non-limiting examples of the gasoline engine/fuel systems include,

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carburetor, improved gasoline, manifold feed/injected, direct injection, direct injected stratified charge, advanced stratified charge, and the like. It is contemplated that Applicant's automotive gasolines will be in combustion systems employing exhaust catalysts (including three way systems), regulated emission control systems, and the like.

One of the particular objects of Applicant's invention is the incorporation of emission catalysts, OBD II catalyst efficiency monitors, related emission control systems in methods, where upon their operation in the presence of a Mn containing combustion exhaust gas, is not impaired.

Another object is the operation of gasoline engines operating under minimum threshold loads, where upon the benefits of Applicant's invention become beneficial. For example, Applicant has discovered that when employing ECS compounds and minor amounts of metallic, e.g. Mn, that optimum fuel economy and temperature reduces do not start to occur until loads are at least 12.5 ihp to 16.0 ihp.

Applicant's co-fuel gasolines should be constructed to minimize hazardous pollutants to the maximum extent possible. Thus, sulfur concentrations should approach sulfur free levels, if possible, harmful heavy aromatics (while their effect is substantially mitigated in the practice of this invention) should be reduced as much as practical. To the extent possible, co-fuels should be formulated to reduce volatile organic compounds (VOC's), NOx, benzene, butadiene, formaldehyde, acetaldehyde,

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polycyclic organic material. Reformulated gasolines constructed under the complex model are expressly contemplated.

5 An important embodiment of Applicant's invention is its capacity towards ultra clean combustion emissions, due to the nature of its combustion. Consequently, in addition to the reduction of most hazardous emissions, it is an embodiment to avoid combustion chamber deposits, which now be caused by the use of detergents to keep intake valves  
10 clean.

An additional embodiment is the reduction of PM 10, which is believed to be caused by heavier aromatics. Applicant's invention is effective to reducing such particulate matter, again due to the unique combustion that  
15 is occurring.

#### Example 98a

A method of operation an internal gasoline combustion engine, said method comprising: mixing a convention, non-  
20 convention, or reformulated gasoline with a combustion improving amount of an ECS compound and a combustion improving amount of MMT and/or other metallic; combusting said fuel in said engine, wherein engine is under load of at least 12.5 ihp (more preferably 16.0 ihp), wherein fuel  
25 economy is increased.

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Example 98b

The method of 98a, wherein the load is approximately 20 ihp and fuel economies are improved 5% to 30% and/or combustion temperature is reduced 50°F to 100°F.

5

Example 98c

The method of 98a, wherein said fuel contains oxygen by weight of 0.05% to 3.7%, supplied by MTBE, ETBE, DMC, methanol, ethanol, or methylal, or mixture, and 1/64 to 1/4 gram Mn/gal of MMT; and wherein engine is operated at load exceeding 16 ihp; whereby fuel economy is improved and/or combustion temperatures are reduced.

10

15

Another object of instant invention is improving burning velocity/combustion temperatures by modifying T-90 and/or end-boiling point distillation fractions enhancing combustion, improving mileage, driveability and/or reducing hazardous combustion emissions.

20

Still another object is improving combustion by controlling mid-range distillation temperatures. Still another is T-10 adjustment to enhance the properties of this invention.

25

RVP reductions are contemplated and it is preferred that Applicant's gasolines generally be lower RVP fuels 4.0 to 12.0 psi, more preferred are those 4.0 to 9.0 psi, 4.0 to 8.0 psi, 4.0 to 7.5 psi, 6.0 to 7.0 psi, 6.0 to 6.5 psi, 1.0 to 6.0 psi, 1.0 to 3.0 psi, 1.0 to 2.0 psi, or lower. Contemplated RVP include 6.4, 6.9, 7.0, 7.1, 7.2

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(max), 7.3 (max), 7.4 (max), 8.3 (max), 7.8, 7.9, 8.0, 8.1  
(max), 8.2 (max), 8.3 (max)

As noted, a principal object of this invention is combustion temperature reduction. It is reported that gasoline's combustion temperature is 2102°C (J.B. Fenn "Fourth Symposium on Combustion," Baltimore, p 231 (1953). Thus, it expressly contemplated that one or more of the means herein cause the reduction of combustion temperatures by at least 25°F, 50°F, 100°F, 125°F, 150°F, 200°F, 250°F, 300°F, 350°F, 400°F, or more.

In the T-10, T50, T-90 temperature reducing or control practices of this invention eliminating gasoline components having low latent heats of evaporation and/or low burning velocities is express contemplated.

It is desireable that high boiling components with latent heats of vaporization of 150 btu/lb or 860 btu/gal, and lower, be reduced or removed from the gasoline composition, when practical.

It is preferred the finished hydrocarbon portion of the gasoline composition (e.g. absent oxygenates and metals, etc.) have an average latent heat of vaporization greater than 150 btu/lb or 860 btu/gal. It is more preferred that it be 160, 170, 180 btu/lb, if practical.

Applicant has discovered modification leading to a higher latent heat of evaporation can be normally be accomplished absent losses in the fuel's heating. Often, heating values increase.



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The preferred practice is removal of higher boiling material (with low latent heats of vaporization and/or low burning velocity) until said oxygen/metals free hydrocarbon composition has an average latent heat of vaporization equal or greater than 880, 890, 900, 905, 910, 915, 920, 925, 930, 940, 950, 970, 990, 1000, 1050, 1100, 1200 btu/gal. It is desireable that it be greater than 900-910 btu/gal, or more. 920 btu/lb being even more preferred. While there is no upper limit to said base (co-fuel's) composition's latent heat of vaporization, economic costs and other practical considerations will control.

Alternatively, it is acceptable that reductions of end point and/or T-90 temperatures be in such an amount that the average latent heat of evaporation of the adjusted fuel (e.g. the reduced fuel), such that its latent heat of vaporization is 0.5% to 10.0%, or greater, than the unadjusted base fuel. Increases of 1.0% to 20%, 40%, or greater are also desireable.

In conventional fuels it is generally preferred that minimum increases in average latent heat of vaporization due to reductions of end/T-90 temperatures and/or due to control of T-50, T-10 temperature (absent use of an ECS compound or azeotroping co-solvent, etc.), be such that addition of 1/32 gram mn/gal of MMT improves fuel economy of same MMT containing fuel unadjusted for T-90. In such circumstances T-90 reduction normally requires a minimum of a 50oF variance between adjusted and unadjusted fuels.

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Applicant has discovered that acceptable T-90 temperatures will range from 240°F, 250°F, 255°F, 260°F, 265°F, 270°F, 275°F, 278°F, 280°F, 285°F, 290°F, 295°F, 300°F, 305°F, 310°F, 315°, 320°F, 325°F, 330°F, 335°F, 340°F, 345°.

5 Temperatures outside these ranges are also contemplated. However temperatures below 280°F are preferred, normally.

Final temperature is function of improved latent heat of vaporization and/or improved combustion velocities, elicited by the reduction, which in turn is dependent upon  
10 the base fuel. Modifying differing fuels (and hydrocarbon streams) will elicit differing response. Thus, variability in actual amount of T-90 reduction is anticipated.

#### Example 99

15 A conventional or reformulated gasoline composition wherein higher boiling point fuel fraction is cut such that end point and/or T-90 boiling temperatures of the gasoline are reduced; whereby the cut clear fuel's average latent heat of vaporization is at least 0.5% and more preferably  
20 1.5%, or greater, than the clear uncut fuel.

#### Example 100

The method of 99, wherein the inclusion of 1/32 gr Mn/gal of MMT shows increase in the cut composition's fuel  
25 economy when compared to uncut fuel (inclusive metallic).

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Example 101

The method of 99, wherein the cut fuel containing metallic is combusted and exhausted through an exhaust catalyst wherein an OBD-II catalyst monitor is employed; whereby manganese oxide deposition on catalyst wash coat are sufficiently controlled that said catalyst monitor does not fail.

Example 102

The method of 99-101, wherein an oxygenated ECS compound is added at 0.5% to 2.7%, 3.0%, 3.5% oxygen to the base fuel, and wherein the resultant T-50 temperature exceeds 155°F, 170°F (175°F desirable) but is less than 220°F and whereby T-90 temperature absent the presence of the oxygenate does not exceed 300°F, and more preferably less than 280°F, 275°F; 270°F and wherein after combustion and emissions are exhausted through an exhaust catalyst where an OBD-II catalyst monitor is employed; manganese oxide deposition upon catalyst wash coat is sufficiently controlled (or virtually non-existent) that said monitor does not fail.

Example 103

The example of 102, wherein said adjusted and unadjusted gasolines both comprise 1.0% to 2.0% oxygen by wt of MTBE and a cyclomatic manganese tricarbonyl having a Mn concentration from 0.001 to 0.03125 gr. mn/gal, such

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that fuel economy of the reduced boiling temperature fuel is improved over the unadjusted fuel.

Example 104

5           The example of 99, wherein T-90 temperatures of the adjusted reformulated fuel is approximately 260°F to 280°F, or less.

Example 105

10           The example of 103-104, wherein MTBE is replaced in whole or part by dimethyl carbonate.

          Limitations on olefins are desirable to reduce smog. Furthermore, limitation on Reid Vapor Pressures (RVP) to for example less than 8.0, 7.5, 7.0, 6.8, 6.5, 6.2, 6.0,  
15   5.8, 5.6 PSI or less and sulphur concentrations to less than 0.002 wt % (including sulfur free compositions), and naphthenes at less than 7% (or less than 0.5%, if practical) by volume are contemplated.

          In the practice of this invention it is contemplated  
20   that gasoline fuels include those generally meeting ASTM D 4814 and related specifications, EPA's simple and complex model reformulated gasoline ("RFG") specifications under Clean Air Act 42 USC 7545 § 211 (k), RFG certifying standards (incorporated by reference), EPA certification  
25   specifications under 42 USC 7525 § 206, any other legal or industry standard, existing and future.

          Thus, it is an embodiment that Applicant's compositions meet current and all future CAA and/or EPA

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environmental/emission standards, including compositional and performance standards.

5 Emissions of some concern to those in the art are volatile organic compounds ("VOC's), which contribute to low altitude ozone formation. VOC's are mostly emitted from the evaporative emissions. Exhaust VOC's attribute to a very minor portion of VOC emissions.

10 Emissions of principle concern include toxic and NOx emissions. Within the context of this invention, said VOC, toxic, NOx and other regulated emissions are defined in accordance with EPA definitions.

15 However, an emission of paramount concern is toxic emissions, which this invention unexpectedly reduces, on a mass basis, on the order of 5%, or more, over conventional and other reformulated gasolines. This is a most unexpected development. For example, it has been found that the levels of 1,3-butadiene (a regulated toxic) increase in the presence of MTBE when reducing olefins and T-90 temperatures. Furthermore, it has been found that 20 formaldehyde exhaust emission actually increase when aromatics are reduced and/or when MTBE is added. Additionally, it has been found that acetaldehyde emissions also increase as aromatics are reduced.

25 For example, it has been found that by increasing the percent of MTBE from 0% to 15% by volume that formaldehyde emission increased 26%. By reducing aromatics from 45% to 20%, 1,3-butadiene increased 11%, and formaldehyde increased 23%, and acetaldehyde increased 19%.

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This is most unfortunate, because in order to meet the requirements under the complex model, refiners must include an oxygenate, MTBE being the most preferred by refiners, and they are additionally required to reduce aromatic emissions. Thus, there is a substantial need to reduce aromatics and/or olefins in the presence of MTBE, absent attendant increases in toxic emissions.

Unfortunately, under the current specifications which require MTBE's presence, fuel economies suffer. Applicant has discovered that introducing MMT while simultaneously reducing end boiling and/or T-90 temperatures, in the manner described herein, Applicant is able to unexpectedly improve fuel economy.

Applicant has also discovered that employing MMT at greater than 1/32 gr. mn/gal improves fuel economy when MTBE concentrations are greater than 2.0% O2 by wt (e.g. 2.7% O2 wt).

However, fuel economies appear to suffer in the presence of MTBE at O2 weight concentrations of less than 2.0% wt (e.g. 1.0%) even with 1/32 gram Mn/gal of MMT. Applicant has discovered that this phenomena to be correlated to T-90 temperatures.

Applicant has found that if T-90 temperatures are not sufficiently reduced (so as to increase the average latent heat of vaporization of the fuel) and/or where an additional enhanced ECS chemistry such as DMC is not present, a 1.0% to 2.0% O2 wt MTBE and MMT of 1/32 gr mn/gal (or less) combination in a reformulated fuel will

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suffer lose in fuel economy, compared to the based gasoline absent the oxygenate (with or with out MMT).

Thus, it is a preferred embodiment to employ MTBE at O<sub>2</sub> concentrations greater than 2.0% weight. If MMT is  
5 employed at 1/32 g Mn/gal or less, it is expressly preferred that T-90 temperatures be reduced to less than 320°F, 300°F, with 280°F being preferred.

Quite unexpectedly, when employing Applicant's invention, namely a combustion improving amount of Mn in  
10 the presence of a combustion improving/temperature reducing ECS compound and/or reduction of T-90 temperatures, the expected reduction in fuel economy is not experienced. To the contrary fuel economy may actually increase. The expected increase of toxic pollutants is also abated.

15 Applicant has further discovered that substituting DMC for MTBE and/or by combining DMC with MTBE, particularly at O<sub>2</sub> wt concentrations of 2.0%, or higher, the substitution unexpectedly operates to further increase mileage and improve emissions.

20 Thus, it is an embodiment of this invention to employ gasolines with reduced aromatic contents, e.g. amounts ranging from 5% to 35% by volume. However, concentrations closer to 20%, 15%, or less are more preferred. Also preferred are reduced concentrations of olefins (e.g. 5% to  
25 10%, less than 8%, 6%, 5% preferred), and especially in fuel fractions with reduced T-90 temperatures (preferably in the range of 300°F to 260°F or less).

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It is contemplated to such hydrocarbon fraction would be added a combustion improving amount of Mn, an oxygenated ECS compound, particularly, MTBE, ETBE, TAME, diisopropyl ether, ethanol, and DMC, including mixtures; whereby the fuel's average latent heat of vaporization exceeded 880, 900, 910 BTU/lb @ 60°F; and whereby subsequent to combustion results in fuel economy improvements and reduced toxic emissions including NOx, HC's, 1,3-butadiene, formaldehyde, and/or acetaldehyde.

Applicant has discovered that it is desireable to reduce MBT spark advances to assure smooth operation, especially as his higher burning velocity gasolines are employed in constant compression ratio engines. With greater increases in burning velocity, greater spark advance decreases are preferred. Acceptable MBT spark advance decreases range from 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 5.5%, 6.0%, 6.5%, 7.0%, 7.5%, 8%, 8.5%, 9%, 9.5%, 10%, 10.5%, 11.0%, 11.5%, 12.0%, 12.5%, 13.0%, 13.5% to 40.0%. Decreases over 0.5%, 2.0%, 5.0% to 10% are more desirable.

Applicant has also discovered that optimum compression ratios due to increased burning velocities and prolonged combustion are those of 8.5:1 to approximately 13.0:1, when for example a 2% O2 by weight DMC and 1/16 gr. Mn/gal MMT gasoline composition are employed. With this combination the more preferred is ratios are 9.5:1 to 12.5:1, with 11.5:1 to 12.5:1 being slightly more preferred. A compression ratio of 10.5:1 is very satisfactory as well



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and is regarded as preferred. Higher concentrations of a ECS fuel comprised of DMC and appropriate concentrations of a metallic lend themselves to higher compression ratios.

5     Example 106

        A novel method of operating an engine comprising: mixing an unleaded gasoline wherein the MTBE represents 2.0% oxygen by weight and MMT is included at 1/32 gr Mn/gal; combusting said fuel in an engine wherein MBT spark  
10     advance has been retarded approximately 1.0% to 2.5% (1.5% preferred); whereby operation of said engine improves thermal efficiency and/or emissions.

Example 107

15     A novel method of operating an engine comprising: mixing an unleaded gasoline wherein DMC represents 2.0% oxygen by weight and MMT is included at 1/32 gr Mn/gal; combusting said fuel in an engine wherein MBT spark advance  
20     has been retarded approximately 2.0% to 10% (8.5% preferred); whereby operation of said engine improves thermal efficiency and/or emissions.

Example 108

        An unleaded, phosphorus free, reformulated gasoline  
25     composition having a max of 7.0 psi RVP, a max of 5.0% vol olefins, a max of 20% vol aromatics (preferably 15%, 10%, or lower), a max of 0.8% benzene (preferably 0.6%, or lower, or benzene free), a max of 100 ppm sulfur

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(preferably 50 ppm or less or sulfur free), an O<sub>2</sub> concentration ranging from 1.8% to 2.2%, 2.0% to 2.7%, or 3.5% O<sub>2</sub> wt of dimethyl carbonate, MTBE, ETBE, TAME, ethyl tertiary amyl ether, diisopropyl ether or ethanol, or mixture, a cyclomatic manganese tricarbonyl compound at 1/64 to 3/16 gr. Mn/gal (1/32 gr mn/gal preferred), a max T-90 temperature of 260°F to 280°F, or less, a T-50 temperature of approx. 160°F to 230°F (170°F to 205°F)., a bromine number of 20 or less; an average latent heat of vaporization of 910 to 930 BTU/gal or more.

#### Example 109

The Example of 106-108, wherein the fuel contains an ashless dispersant, induction control/deposit control additive in conformity with § 211 (1) and appropriate regulations of the Clean Air Act; and optionally containing a minor amount of a co-solvent to enhance water solubility, such as hexanol.

#### Example 110

The examples of 106-108, wherein the fuel's T-90 temperature is no greater than 300°F, preferably 280°F, or less, T-50 temperature after inclusion of MTBE at 2.0% to 2.7% is greater than 170°F but less than approximately 200°F; whereby warm weather driveability does not suffer; and wherein the fuel's latent heat of evaporation is greater than 900 btu/gal, more preferably 905 btu/gal, and the Mn concentration is 1/32 gal; whereby said combustion

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of said fuel does not contribute to the failure of OBD-II catalyst oxygen sensors.

Example 111

5           A method for avoiding the failure of OBD-II exhaust gas oxygen sensor; said reducing T-90 of target gasoline whereby result fuel's average latent heat of vaporization is increased an amount sufficient to reduce combustion temperature by at least 15°F or more and/or to measurably  
10   increase average burning velocity as measured by a laminar bunsen burner; combining said fuel with MTBE at 1.2% to 2.7% weight; whereby the composition's T-50 temperature is at least 170°F (preferably greater than 175°F and less than 210°F, 200°F); combusting said fuel in an engine and  
15   emitting the resultant exhaust for an extended period through a three-way exhaust catalyst system equipped with an ODB-11 catalyst efficiency monitor; whereby manganese deposition upon the catalyst wash coat is insufficient to cause the failure of said sensors.

20

Example 112

          The method of 111, said fuel's T-90 temperatures are approximately 300°F, and more preferably approximately 280°F or less, and/or wherein the measurable increase in burning  
25   velocity was at least 1.0%, or greater, than the unadjusted fuel.

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Example 113

The methods of 111-112, wherein the fuel is absent the oxygenated compound.

5     Example 114

The method of examples 113, wherein engine operation is for a period of 5,000; 20,000; 50,000; 75,000; or 100,000 miles

10    Example 115

The Examples of 106, 107, 108, 110, 111, wherein the average burning velocity of the composition as measured in a laminar bunsen burner at ambient conditions is greater than 46, 48 cm/sec, more preferably 50 cm/sec or greater  
15    (using methanol at 57.2 cm/sec as bench mark).

Example 116

The Example of 106-107, wherein the particle size of the fuel injected into the combustion chamber is less than  
20    70 microns, more preferably less than 50 microns.

Example 117

The Example of 106-107, wherein the injected fuel particle has an approximate injected pressure of  
25    approximately 15 to 45 psi.

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Example 118

The example of 106, 107, 111, wherein the temperature of combustion is sufficiently reduced that under for example a load of 20 indicated horse power exhaust gas temperatures are reduced by at least 10°F to 50°F (or more), whereby the average exhaust gas temperature entering the exhaust gas inlet is less than 1400°F (or such other temperature that manganese oxide coating of the catalyst wash coat does not appreciably occur).

Example 119

The examples of 106, 107, wherein reduced temperature engine exhaust gases are vented through an exhaust emissions catalyst and the emission system's onboard catalyst monitoring does not fail due to false catalyst oxygen storage capacity readings.

Example 120

The examples of 106, 107, 108, 110, wherein such method qualifies for an EPA waiver under § 211 (k) of the Clean Air Act.

Example 121

A low toxic fuel economy improving composition comprising an unleaded fuel composition comprising phosphorus free hydrocarbons, having a max of 8.0, 7.0, 6.5, or 6.0 psi RVP; a max of 6.0%, 5.0% vol olefins, a max

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of 25%, 20% vol aromatics (preferably 15%, 10%, or lower),  
a max of 0.8% benzene (lower or benzene free) a max of 40  
ppm sulfur (lower or sulfur free), a total O2 concentration  
ranging of 1.0 to 2.7% wt or 3.5% O2 wt of dimethyl  
5 carbonate, MTBE, ETBE, TAME, or ethanol, a cyclomatic  
manganese tricarbonyl compound at 1/64 to 3/16 gr. Mn/gal  
(preferably 1/32 gr. Mn), a max T-90 temperature of 300°F,  
280°F (preferred), a T-50 temperature of approx. 170°F to  
230°F., a minimum (R+M)/2 octane of 87, a bromine number of  
10 20 or less, an average latent heat of vaporization of 900,  
910, 920 or more BTU/gal at 60°F; a heating value greater  
than 106,000 btu/gal at 60°F (more preferably greater than  
108,000, 114,000 btu/gal); whereby toxic emissions of 1,3-  
butadiene, formaldehyde, or acetaldehyde emissions are  
15 reduced and/or fuel economy is improved.

Example 122

The Example of 121, wherein the oxygenate is MTBE at  
2.0% wt and the average latent heat of vaporization of the  
20 fuel exceeds 900 BTU/gal @ 60°F and is preferably greater  
than 905 BTU/gal @ 60°F; MMT concentration is 1/32 gr./gal;  
and average heating value of the composition exceeds  
106,000 btu/gal at 60°F; has an average laminar burning  
velocity of at ambient conditions greater than 48 cm/sec.

25

Example 123

The MTBE composition of example 122, wherein the MMT  
concentration is greater than 1/32 gr mn/gal.

Example 124

The examples above, wherein the oxygenate is DMC and the MMT concentration is greater than 1/32 gr mn/gal.

5

Example 125

The composition of examples 108, 121, wherein RVP is 6.8, 6.5, 6.0, 5.5 psi or lower.

10 In the practice of this invention, in view of reducing regulated emissions, preferred gasoline compositions include, but are not limited to those which have the following specifications:

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TABLE 6

LEAD FREE FUELS

	<u>A</u>	<u>B</u>	<u>C</u>
Reid Vapor Pressure (max psi)	8.7	7.0	3.0-6.0
Olefin (max volume %)	9.2	8.0	0.0-8.0
5 Aromatics (max volume %)	32.0	20.0-25.0	0.0-10.0
Benzene (max volume %)	1.5	1.0	0.0-0.5
Sulphur (max parts/million)	339	100	0.0-10
Oxygen (weight %)	0.0	2.0-2.7	2.0-5.0
T-90 (Max temperature °F)	330.0	320.0	300-330
10 (R & M)/2 (min)	87.0	87.0	87.0-95.0



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Example 126

The fuels of B and C of TABLE 6 above, wherein 1) said fuels contain Applicant's oxygenated means and a 2) combustion improving amount of manganese, and 3) wherein the combined evaporative emissions of said fuels' storage and its delivery to a combustion chamber, and emitted atmospheric combustion emissions, are 4) such that in the year 1995 said fuel's volatile organic compound emissions and toxic air pollutants, on a mass basis, are 15% lower than the baseline gasoline as defined under § 211 (k) of the Clean Air Act, and are 5) such that in the year 2000 said fuel's volatile organic compound emissions and toxic air pollutants, on a mass basis, are 25% lower than said baseline gasoline.

Example 127

An unleaded, phosphorus free, reformulated gasoline composition fuels having a max of 8.0, 7.2, 7.0, 6.5 psi RVP, a max of 8.0%, 6.0% vol olefins, a max of 20-25% vol aromatics, a max of 1%, 0.8% benzene (preferably less), a max of 300-40 ppm sulfur (preferably lower or sulphur free), an O2 concentration ranging from 2.0 to 2.7% wt or 3.5% O2 by weight of dimethyl carbonate, a cyclomatic manganese tricarbonyl compound or mixture at 1/64 to 3/16 gr. Mn/gal (preferably greater than 1/32 gr/gal), a max T-90 temperature of 300°F to 320°F (preferably 280°F or lower), a preferred T-50 temperature of approx. 170°F to 220°F; a minimum latent heat of vaporization of 900, 905 BTU/gal @

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60°F (preferably greater than 920 BTU/gal @ 60°F ); a minimum heating value of the composition assuming 2.0% O<sub>2</sub> weight of 106,000 BTU/gal @ 60°F, and a minimum average laminar burning velocity at ambient conditions of 48 cm/sec (50 to 52 cm/sec or more preferred).

Example 128

The above example wherein the composition additionally contains deposit control additives in conformity with § 211 (1) and related Sections/regulations of the Clean Air Act.

Example 129

Example 127, wherein the composition optionally contains at least one C<sub>4</sub> to C<sub>6</sub> alcohol or other additive assuring hygroscopic stability (water solubility).

Example 130

The examples of 106, 107, 111, wherein the fuel injection system injects a fuel vapor under acceptable pressure into a combustion chamber, wherein average vapor particle sizes are less than 60 microns, wherein an EGR system, an onboard oxygen sensor, and injection sensors are employed; whereby fuel economy is improved by at least 2%.

Example 131

The examples of 106, 107, 111, wherein the fuel injection system injects a fuel vapor under optimum

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pressure into a combustion chamber, wherein average vapor particle sizes are 10, 20, 30, or 40, wherein a turbocharger, EGR system, an onboard oxygen sensor, and injection sensors are simultaneously employed; whereby fuel economy is improved by at least 2%.

#### Example 132

The examples of 106, 107, 111, wherein the combustion chamber is designed to increase turbulent burning velocity.

#### Example 133

The examples of 106, 107, 111, 127, wherein the combustion chamber is designed to increase turbulent burning velocity, and wherein the compression ratio is 2.0:1 to 6.5:1; 7.5:1, 8.0:1, 8.5:1; 9.0:1; 9.5:1, 10:1, 10.5:1, 11.0:1, and more preferable 11.5:1.

#### Example 133a

The examples of 107, 127, wherein dimethyl carbonate is employed and the compression ratio ranges from 9.5:1 to 12.5:1.

#### Example 134

The examples of 106, 107, 111, wherein the combustion chamber is designed to increase turbulent burning velocity, and wherein the compression ratio exceeds 17:1.

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Example 135

The examples of 106, 107, 111, wherein the combustion system operates in conjunction with a regulated exhaust/emission control system employing an emission catalyst and an on-board oxygen sensor.

Example 136

A method of operation, wherein at least 30% of the U.S. automotive fleet operates on said fuels, whereby total reference concentrations of air borne manganese emitted from such operation, does not exceed 0.05 ug/m<sup>3</sup> or EPA standards, which ever is lower.

Applicant's gasoline compositions expressly contemplate reductions in emissions and compositional characteristics as set forth in Tables 7 and 8, below.

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TABLE 7

COMPLEX MODEL STANDARDS FOR RFG

5			
	PROPERTIES	PHASE 1 1995	PHASE 2 2000 and after
10	VOC REDUCTION (%) /GAL(1)		
	Class B	35.1	27.5
	Class C	15.6	25.9
15	NOx REDUCTION (%) (1)		
	Summer	0-1.5	5.5-6.8
	Winter	0-1.5	0-1.5
20	TOXICS REDUCTION(1)	15.0-16.5	20.0-21.5
	OXYGEN (WT%)	2.0-2.1	2.0-2.1
	BENZENE (vol%)	0.0-1.0	0.0-1.0
25			
30	Note 1	Reductions are from the baseline gasoline defined under § 211 (k) (10) (B)	

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TABLE 8

## 5 EXAMPLE FUELS COMPLYING WITH CLASS C RFG REGULATIONS

10	PROPERTIES	PHASE 1 1995-2000	PHASE 2 2000 and After
----	------------	----------------------	---------------------------

## REDUCTION % (1)

15	VOC'S	17.3	27.6
	NOX	1.6	6.9
	TOXICS	25.4	27.6

## 20 PROPERTIES

20	RVP (psi)	8.0	6.6
	OXYGEN (WT%) (2)	2.1	2.1
	AROMATICS (VOL%)	25.0	24.0
	BENZENE (VOL%)	0.95	0.95
25	OLEFINS (VOL %)	9.2	9.2
	SULPHUR (ppm)	339	185
	E200	41.0	45.0
	E300	83.0	87.0
30	Manganese (Gr. Mn/g) (3)	1/32	1/32

35 Note 1 Reductions are from the baseline gasoline defined under § 211 (k) (10) (B)

Note 2 In the form of dimethyl carbonate.

40 Note 3 Manganese concentrations may range from 1/64 to 1/4 gr. Mn/gal.

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In the practice of this invention, when formulating gasoline compositions to meet RFG standards, tailoring may be required. It has been found that various components, which have the largest effect in reducing specific target emissions may be tailored:

VOC's: RVP, Aromatics, Sulphur

NOx: Sulphur, Aromatics, Olefins; and

Toxics: Benzene, Aromatics, oxygen

In the practice of this invention ECS oxygenates with methyl groups, such as methanol, diMethyl carbonate, MTBE and TAME, and the like, appears to have slightly better capability of reducing toxic emissions than do those with ethyl groups, such as ethanol, ETBE, etc.

In the formulation of conventual or RFG fuels, reductions in Reid Vapor Pressure (RVP) have significant effect in reducing VOC emissions. In the practice of this invention, Reid Vapor Pressure ("RVP") reductions of the resultant fuel composition to 7.0, 6.5, 6.0, 5.5, 5.0, 4.5 psi, or lower, are preferred.

RVP is the strongest predictor of evaporative VOC emissions and RVP reductions represents the best means of reducing evaporative VOC emissions, on a mass basis, as defined by EPA. For example, a reduction of RVP from 8.7 psi to 6.5 psi reduces (on a mass basis) VOC emissions approximately 23%, reduces toxic emissions about 4%, and reduces NOx emissions about 0.5%.

Oxygen increases in the fuel strongly reduce toxic emissions. It appears that there is a linear relationship

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to weight increases in oxygen content and reductions in toxic emissions. Increases in O<sub>2</sub> content appears to be one of the strongest predictors of reducing toxic emissions. For example, an increase of O<sub>2</sub> from 0% to 3.5 wt% reduces toxic emissions about 11%.

Reformulated fuel regulations recognized that O<sub>2</sub> concentrations above 2.7% weight, particularly MTBE directly increased NO<sub>x</sub> emissions. Applicant has quite unexpectedly discovered in the practice of his invention that O<sub>2</sub> wt % concentrations above 2.7% wt. are quite able to control expected NO<sub>x</sub> increases. This is illustrated in Figure 6, which shows that burning velocity increases of oxygenated fuels including O<sub>2</sub> content as high as 4.2% (methanol/ethanol-MEOH fuel) had substantially reduced NO<sub>x</sub> emission as burning velocity increased. It appears this phenomena is also a function of combustion temperature. For example Figure 3 illustrates that at the low combustion temperatures, independent of O<sub>2</sub> concentration, NO<sub>x</sub> emissions declined. If anything, higher concentrations of O<sub>2</sub> yielding greater reductions in combustion temperature appears to be the principal agent of Applicant's invention in reducing NO<sub>x</sub> emissions. Thus, it is Applicant's preferred practice to employ at least 1.5% or greater oxygen by wt., permitting optimal combustion with Mn at 1/32 gr/gal or greater. Oxygen Concentrations below 1.5% to 2.0% do not optimize Applicant's invention.

Thus, it is possible in the practice of this invention to include appreciably higher concentrations of O<sub>2</sub> in RFG



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fuel's (beyond those even permitted under current rules) to reduce NOx, toxic emissions, absent expected reductions in fuel economy and increases in NOx emissions, etc..

Thus, it is an embodiment of this invention to employ  
5 O2 concentrations greater than 2.0%, 2.1%, 2.7%, 3.5%, 4.0% or even 5%, 6%, or more, by weight.

Reductions in aromatics strongly influence reductions in toxic, VOC, and NOx emissions. Reductions appear to be linear, with toxic emissions being the most significantly  
10 influenced, with reductions in toxics similar to those experienced with reductions in benzene and/or increases of O2 content. For example, a reduction of aromatics from 33% to approximately 10% vol. reduces toxic, NOx, and VOC emissions by about 17%, 7%, 6%, respectively.

15 A desirable RFG aromatic content, in the practice of this invention is less than 25%, 20% preferred, with 18% to 10% particularly preferred.

However, as noted above, when achieving higher burning velocities at low or lower combustion temperature as  
20 contemplated in the practice of this invention, RFG fuels with aromatic concentrations higher than those believed acceptable or even higher than those permitted by regulation, still achieve appreciable reductions in toxic and other emissions associated with aromatics.

25 These reductions are material, unexpected, and well beyond those otherwise achievable in the formulation of standard RFG fuels.

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Accordingly, aromatic concentrations higher than those now believed unacceptable in meeting RFG emission standards may be ultimately employed, while still achieving the performance and/or emission standards imposed by law.

5        Reductions in benzene concentrations are believed to directly and linearly influence reductions in toxic emissions. For example, a reduction of benzene from 1.5% vol to 0.5% vol reduces toxic emissions on the order of 17%. Thus, benzene reductions, like increases in O2 content, 10 represent one of the strongest predicator for reducing toxic emissions. Preferred benzene concentrations are less than 1.0% by volume with most preferred concentrations approaching 0%.

15        However, like aromatics, benzene concentrations higher than permitted by current regulations, can be employed in the practice of instant invention while none-the-less achieving appreciable toxic and other emissions reductions, beyond those otherwise achievable under the current formulation specifications of RFG fuels. This is again is 20 most unexpected. Accordingly, benzene concentrations higher than those now believed acceptable in meeting RFG emission standards may ultimately be employed to meet performance and/or emission standards.

25        Reductions in sulfur content linearly influence reductions in NOx, toxic, and VOC emissions (in order of their relative % emission reductions). For example, a reduction in sulfur from 340 ppm to approximately 50 ppm causes a reduction of NOx, toxic, and VOC emissions of

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about 11.0%, 8.5%, and 3.5%, respectively. It appears that reductions in NOx emissions are strongly influenced by reductions in sulfur content. In the practice of this invention sulfur concentrations less than 40 ppm are particularly preferred. Sulfur content 30 ppm or less (or sulphur free) is even more preferred. Again, the operation of this invention will permit environmentally acceptable NOx, Toxics, and VOC's even at sulfur concentrations higher than currently permitted under the regulations.

However, sulfur concentrations on the order of 200 ppm or more appear to be acceptable, due the increased burning velocity and reduced combustion temperatures of instant invention, which appear to inhibit sulfur's adverse NOx and Toxic emission characteristics.

Reductions in olefin concentrations below approximately 9.5% causes modest reductions in NOx and toxic emission's, but modest increases in VOC emissions. Olefin increases above 9.2% to 9.5% show modest reductions in VOC s, but also modest increases of toxic and NOx emissions. Thus, it appears the optimal olefin concentration is about 9.2% - 9.5% volume. However, emission increases due to olefin concentrations less than or greater than 9.2% - 9.5% is not appreciable when compared to the % reductions of the same emissions due to reductions, for example, in aromatic concentrations.

Thus, reductions in olefinic content below 9.2% volume are acceptable and desireable, especially if aromatic concentrations are simultaneously reduced. In other words,

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olefinic reductions are desireable below 9.2% volume, if the RVP or aromatic content reduction offset increases in VOC's. Again, the accelerated burning temperature reducing operation of Applicant's invention appreciably offset such increases. Thus, olefinic contents outside regulatory compositional standards may be employed while meeting performance and emission requirements.

Reduction of E200 temperatures, or that fraction of the distillation, which boils at 200°F, positively reduces VOC and Toxic emissions. In other words, as the E200 temperatures reduce, or as that fraction of the fuel distillation fraction increases above approximately 41%, reductions in VOC and toxic emissions are experienced. However, an increase in NOx emissions are also experienced. As E200 fraction increases, say from 42% to 60%, VOC and toxic emissions are reduced approximately 3.0%-4.0%, but NOx emissions increase approximately 2.0%. However, significant reductions of these emissions occur non-the-less, independently of such modification.

Applicant believes too high an E200 fraction (translating into too low of a T-50 temperature) has its draw backs, as warm weather driveability is impaired when T-50 fractions are below 170°F, especially when O2 content is 1.0%, 2.0%, or greater. Such impaired driveability, due to difficulty in restarting engines, ect., perhaps creates more harmful emissions than the modest reductions otherwise achieved. Thus, it is an embodiment of this invention to

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construct Applicant's T-50 temperatures above 170°F, 175°F, 180°F, 185°F, 190°F where practical.

When the E300 fraction increases from 84% to 95% of the fraction, VOC and NOx emissions are modestly reduced approximately 2.0% and 0.5%, respectfully. Toxic emissions increase approximately 1.5%. The modest gains appear hardly worth the cost.

However, with the operation of Applicant's combustion improving temperature reducing means, such toxic increases are mitigated and the advantage of higher average latent heat of vaporization fuel enhances MMT.

In the practice of Applicant's invention it is expressly contemplated that the base RFG gasoline composition be tailored in a number of regards. For example, it may be tailored to eliminate virtually all polynuclear aromatics, all C10+ aromatics, such as naphthalene, pyrene, and anthracene, and the like. It may be tailored to eliminate known component toxics such as 1,3-butadiene and the like. The composition may also be tailored to reduce low burning velocity material, low latent heat of vaporization, and/or low specific heat components. This practice may also be employed with other fuels of Applicant's invention, including for example, Jet Aviation, No. 2. and No. 6 fuel oils.

Applicant's most preferred Mn. concentrations ranges for unleaded gasolines, including aviation gasolines, reformulated gasolines are above 1/32 gr, 1/16 gr to approximately 3/8 gr Mn/gal. A manganese concentration of

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1/32 gr Mn/gal is particularly preferred as representing one of the best antiknock values for the cost per gram of Mn. However, it is at a lower limit of acceptable environmental concentrations, if oxygenated ECS compounds are employed, especially at oxygen concentrations exceeding 2% weight.

Absent the employment of ECS oxygenated compounds, but employing for example mechanical means, such as improved atomization and/or lower combustion temperature gasolines, and the like, having for example, reduced T-90 temperatures (and/or reduced aromatics), 1/32 gr Mn/gal may be acceptable in controlling HC emission's.

While the current practice of Applicant's invention contemplates the minority usage of ECS fuels in combination with gasoline co-fuels, it is contemplated that advanced applications will include majority usage of ECS and or neat usage in gasoline applications. Thus, it is an embodiment to employ a composition containing a majority of dimethyl carbonate, a combustion improving amount of CMT, and a minority amount of a gasoline co-fuel.

Applicant's gasolines and other co-fuels, to the extent environmental feasible, may further or alternatively contain antiknock quantities of other agents, such as cyclopentadienyl nickel nitrosyl, N-methyl aniline, N-methyl aniline, and the like. Known anti-knock promoters may be employed. 2.4 pentanedione may also be included.

The fuel should contain dispersants, detergents, emulsifiers, metal deactivators, aromatic amines,

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supplemental valve and valve seal recession protectants. Non-limiting examples of such additives include boron oxides, bismuth oxides, ceramic bonded  $\text{CaF}_2$ , iron phosphate, tricresylphosphate, and sodium based additives, and the like.

The fuel may also contain antioxidants, non-limiting examples include, 2,6 di-tert-butylephenol; 2,4,6-tri-tert-butylephenol; 4-methyl-2,6 di-tert-butylephenol; 2-tert-butylphenol, and mixtures thereof; 2,6-di-tert-butyl-p-cresol; and phenylenediamines such as N-N'-di-sec-butyl-p-phenylenediamines; N-isopropylphenylene diamine; and N,N'-disalicylidene-1, 2-propanediamine; and mixtures of tertiary butylated phenols, and/or aromatic amine antioxidants, and mixtures thereof.

It is contemplated the fuel will contain deposit control additives, non-limiting examples include polyether amine, polyalkenyl succinimide, or polyalkenyl succinimide, hydrocarbyl carbonates, such as polybutene alcohol, polybutene chloroformate, polybutene amines formulated in mineral or other carriers, polyisobutylene amine reformulated in polyether carriers, and one-component polyether amines, and the like. Several others have been set forth elsewhere in the specification and are contemplated in gasolines, and other co-fuels. Likewise these and other additives herein are also contemplated in gasolines, as well. It is contemplated the fuel may contain one or more ashless detergents, non-limiting examples including polyether amines, polyalkenyl amines, alkenyl

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succinimides, polyether amide amines, and the like. The fuel may contain such additives as F310, polybutene amines, aminated or polymerized detergents, and the like.

5 The fuel may also contain dissipation static electricity additives. It is contemplated in the practice of applicant's invention that his ECS fuel tends to reduce static electricity concerns to a certain extent. The fuel may contain corrosion inhibitors and the like.

10 The fuel base may contain hydrocarbons boiling outside normal gasoline fuel ranges, which are modified to acceptable gasoline ranges.

#### Aviation Gasoline

15 The invention also contemplates aviation gasoline co-fuel applications and resultant fuels meeting ASTM D 910 specifications (see TABLE 9), especially those that are lead free. However, unlike other embodiments of Applicant's invention, while less preferred aviation gasolines may contain lead. However, Applicant's preferred embodiment is  
20 lead free.

Applicant's invention contemplates a broad application in aviation gasolines for civil and military use, including those applications, which do not comply with ASTM standards. Thus, TABLE 9 is intended to define aviation  
25 gasoline suitable for most types of spark-ignition aviation engines; however, certain equipment or conditions of use may require fuels having other characteristics.



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The principal advantage of Applicant's invention is that it radically improves the thermal efficiency or useful amount of work available from a given amount of fuel. Increases of over 2.0%, 5.0%, 7.5%, 10.0% or more are not unusual. Thus, the flight range of an aviation gasoline powered aircraft employing Applicant's invention should be extended 2% to 30%, or more, depending upon application.

Three principal grades of aviation gasoline contemplated by this invention, which meet ASTM standards, include: Grade 80, Grade 100 and Grade 100LL.

Grades 100 and 100LL represent two aviation gasolines identical in anti-knock quality but differing in maximum lead content and color. The color identifies the difference for engines that have a low tolerance to lead.

Although the grade designations show only a single octane

TABLE 9

## ASTM D 910

5 DETAILED REQUIREMENTS<sup>4</sup> FOR AVIATION GASOLINES<sup>W</sup>

	Grade 80	Grade 100	Grade 100LL	ASTM Test Method <sup>B</sup>
10				
Knock value, min, octane number, lean rating	80	100	100	D 2700 <sup>C</sup>
Knock value, min, rich rating:				
Minimum octane number	87			D 909
15 Minimum performance number <sup>O,P</sup>		130	130	D 909
Color <sup>D</sup>	red <sup>E</sup>	green	blue	D 2392
Dye content:				
Permissible blue dye, <sup>F</sup> max, mg/gal	0.5	4.7	5.7	
Permissible yellow dye, <sup>G</sup> max, mg/gal	none	5.9	none	
20 Permissible red dye, <sup>H</sup> max, mg/gal	8.65	none	none	
Tetraethyllead, <sup>I</sup> max, mL/gal	0.5 <sup>E</sup>	4.0	2.0	D 2559 or D 3341
Requirements for all Grades				
25 Distillation temperature, °F (°C):				
10 % evaporated, max temp	167 (75)			D 86
40 % evaporated, min temp	167 (75)			
50 % evaporated, max temp	221 (105)			
90 % evaporated, max temp	275 (135)			
30 Final boiling point, max, °F (°C)	338 (170)			
Sum* of 10 and 50 % evaporated temperatures, min, °F (°C)	307 (135)*			
Distillation recovery, min, %	97			
Distillation residue, max, %	1.5			
35 Distillation loss, max, %	1.5			
Net heat of combustion, <sup>J</sup> min, Btu/lb	18 720			D 1405 or D 3338
Vapor pressure:				
min, psi (kPa)	5.5 (38)			D 323 or D 2551
max, psi (kPa)	7.0 (49)			D 323 or D 2551
40 Copper strip corrosion, max	No. 1			D 130
Potential gum (5-h aging gum), <sup>K</sup> max, mg/100 mL	6			D 873
Visible lead precipitate, <sup>L</sup> max, mg/100 mL	3			D 873
Sulfur, wt max, %	0.05			D 1266 or D 2622
Freezing point, max, °F (°C)	-72 (-58)			D 2386
45 Water reaction	volume change not to exceed $\pm 2$ mL			D 1094
Permissible antioxidants, <sup>M</sup> max, lb/1000 bbl (42 gal)	4.2			

50 <sup>4</sup> Requirements contained herein are absolute and are not subject to correction for tolerance of the test methods. If multiple determinations are made, average results shall be used.

<sup>B</sup> The test methods indicated in this table are referred to in Section 9.

<sup>C</sup> The values shown in Table 1 represent Aviation Method Ratings. Motor octane ratings obtained by Test Method D 2700 should be converted to aviation ratings by Conversion Table 2.

55 <sup>D</sup> These colors have been approved by the Medical Director Chief, Division of Occupational Health, U.S. Department of Health, Education and Welfare.

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TABLE 9  
(continued)

60

ASTM D 910

DETAILED REQUIREMENTS<sup>4</sup> FOR AVIATION GASOLINES<sup>N</sup>

65 <sup>E</sup> If mutually agreed upon between the purchaser and the supplier, Grade 80 may be required to be free from tetraethyllead. In such a case, the fuel shall not contain any dye and the color as determined in accordance with Test Method D 156 shall not be darker than +20.

<sup>F</sup> The only blue dye which shall be present in the finished gasoline shall be essentially 1,4-dialkylamino-anthraquinone.

70 <sup>G</sup> The only yellow dyes which shall be present in the finished gasoline shall be essentially p-diethylaminoazobenzene (Color Index No. 11021) or phenol, 2,2'-[3,3'-dimethyl][1,1'-biphenyl]-4,4'-diyl]bis(azo) bis [4-nonyl] (Color Index Solvent Yellow No. 107), or 1,3-Benzenediol, 2,4-bis [(alkylphenyl)azo-].

75 <sup>H</sup> The only red dyes which shall be present in the finished gasoline shall be essentially methyl derivatives of azobenzene-4-azo-2-naphthol (methyl derivatives of Color Index No. 26105) or alkyl derivatives of azobenzene-4-azo-2-naphthol.

80 <sup>I</sup> The tetraethyllead shall be added in the form of an antiknock mixture containing not less than 61 weight % of tetraethyllead and sufficient ethylene dibromide to provide two bromine atoms per atom of lead. The balance shall contain no added ingredients other than kerosine, and an approved inhibitor, and blue dye, as specified, herein.

<sup>J</sup> Use the value calculated from Table 1 in Test Method D 1405. Test Method D 2382 may be used as an alternative method. In case of dispute, Test Method D 2382 must be used. In this latter case, the minimum values for the net heat of combustion in Btu's per pound shall be 18 700 for Grades 80, 100, and 100LL.

85 <sup>\*</sup> Note that the temperature conversion for the sum is  $C_1 + C_2 = 5/9 (F_1 - 32 + F_2 - 32)$ .

90 <sup>K</sup> If mutually agreed upon between the purchaser and the supplier, aviation gasoline may be required to meet at 16-h aging gum test (Test method D 873) instead of the 5-h aging gum test. In such a case, the gum content shall not exceed 10 mg per 100 ml and the visible lead precipitate shall not exceed 4 mg per 100 mL. In such fuel the permissible antioxidants shall not exceed 8.4 lb per 1000 bbl (42 gal).

<sup>L</sup> The visible lead precipitate requirement applies only to leaded fuels.

<sup>M</sup> Permissible antioxidants are as follows:

95 N,N'-diisopropyl-para-phenylenediamine  
N,N'-di-secondary-butyl-para-phenylenediamine  
2,4-dimethyl-6-tertiary-butylphenol  
2,6-ditertiary butyl-4-methylphenol  
2,6-ditertiary butylphenol  
75% min 2,6-ditertiary butylphenol plus 25% max tertiary and tritertiary butylphenols  
75% min di- and tri-isopropyl phenols plus 25% max di- and tri-tertiarybutyl phenols

100 These inhibitors may be added to the gasoline separately or in combination, in total concentration not to exceed 4.2 lb of inhibitor (not including weight of solvent) per 1000 bbl (42 gal).

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rating for each grade, each grade must meet a minimum lean mixture aviation rating and a minimum rich mixture super-charge rating.

5 Aviation gasoline, except as otherwise specified in this specification, shall consist of blends of refined hydrocarbons derived from crude petroleum, natural gasoline, or blends thereof with synthetic hydrocarbons or aromatic hydrocarbons, or both.

10 Additives other than tetraethyl lead, dyes, and antioxidants specified in Table 9 are permitted under 5.1 and Section 7 of ASTM specification D 910. These include fuel system icing inhibitor and special purpose additives.

15 Ethylene Glycol Monomethyl Ether, (EGME) conforming to the requirements of ASTM Specification D 4171 (Note 1), may be used in concentrations of 0.10 to 0.15 volume %. 1-Ethylene glycol monomethyl ether, and isopropyl alcohol, and diethylene glycol monomethyl ether of suitable quality as described in ASTM Specification D 4171, may also be employed.

20 Examples of the aviation gasolines contemplated in the practice of this invention and their requirements are set forth in Table 9.

25 It is contemplated that the aviation gasoline of this invention shall be free from water, sediment, and suspended matter. The odor of the fuel shall not be nauseating or irritating.

Similar to automotive applications, knock is to be avoided this aspect of Applicant's invention. Thus. fuel-

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air mixtures in the cylinder of a spark-ignition engine will, under certain conditions, ignite spontaneously in localized areas instead of progressing from the spark. This may cause a detonation or knock, usually inaudible in aircraft engines. This knock, if permitted to continue for more than brief periods, may result in serious loss of power and damage to or destruction of the aircraft engine. When aviation gasoline is used in other types of aviation engines, for example, in certain turbine engines where specifically permitted by the engine manufacturers, knock or detonation characteristics may not be critical requirements. Thus, Applicant's aviation gasolines are sensitive to anti-knock ratings and due attention must be accorded.

Applicant's invention is to apply to Aviation gasoline grades identified by two numbers separated by a hyphen (-) or sometimes a slant line (/). The first number is called the "lean mixture rating" and the second number is called the "rich mixture rating." This specification describes three grades of aviation gasoline as follows: 80-87, 100-130, and 100-130LL. Numbers below 100 are octane numbers, while numbers above 100 are performance numbers. At 100, octane number and performance number are equal. The suffix LL describes a grade containing lower tetraethyllead than a second grade of identical lean and rich mixture ratings. The lean mixture rating together with the rich mixture rating can be used as a guide to the amount of knock-

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limited power that may be obtained in a full-scale engine under cruise (lean) and take-off (rich) conditions.

It has been observed that when isopropyl alcohol (IPA) is added to Grade 100 aviation gasoline as a fuel system icing inhibitor, the anti-knock rating of the fuel may be significantly reduced. Since isopropyl alcohol is normally added in the field at the point of use, the operator is cautioned that performance numbers on the alcohol-fuel blend may not meet specification minimums. Typical performance number reductions with addition of 1 volume % IPA has been about 0.5 performance number on the lean rating and 3-3.5 performance number on the rich rating. Thus a Grade 100 aviation gasoline, rated in the knock test engines at point of manufacture to be 100/130 performance number, might with addition of 1.0 % alcohol be about 99.5/127 performance number. At 3 volume %, the reductions are about 1.5 and 7.5 performance numbers for lean and rich ratings, respectively. Such application of IPA additive may increase the octane rating.

To the extent possible lead usage should be mitigated or not used in the practice of Applicant's invention.

The aviation gasolines of Applicant's invention shall include a minimum net heat of combustion of 18,720 min BTU/lb. Applicant has discovered that heats greater than 18,000 BTU/lb particularly beneficial in the object of enhancing power generation, but given the nature of Applicant's invention and strict ASTM standards, lower

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heating values are acceptable, and in certain applications more desirable.

5 In many spark-ignition aviation engines the gasoline is metered in liquid form through the carburetor where it is mixed with air and vaporized before entering the supercharger from which the fuel-air mixture enters the cylinder of the engine. In other types of engines the fuel may be metered directly into the supercharger or the cylinder or the combustor. The volatility, the tendency to  
10 evaporate or change from a liquid to a gaseous state, is an extremely important characteristic of aviation fuel. It is preferred that the atomization principle set forth above be applied herein.

The preferred maximum vapor pressure of Applicant's  
15 aviation gasoline should be not higher 7 psi (kPa).

The distillation proportions of Applicant's aviation gasoline shall generally comply with ASTM standards. A maximum value is set at 167° F for the 10 % evaporated point to ensure ease of starting and a reasonable degree of  
20 flexibility during the warm-up period. To guard against too high a volatility which might lead to carburetor icing or vapor lock, or both, a minimum value of 307°F is required for the sum of the 10 and 50 % evaporated points.

The minimum value of 167° F for T-90 is contemplated to  
25 control indirectly specific gravity and consequently carburetor metering characteristics.

However, boiling point modification within this requirement is contemplated and T-90 temperature reductions

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are expressly contemplated to improve combustion features and/or increase burning velocity.

Example 137

5           An aviation gasoline comprising a hydrocarbon base, a minimum octane or performance number of 87 or 130, a distillation fraction wherein the sum of the T-10 plus T-50 fractions are 307°F, the T-40 temperature is 167° F and the T-90 temperature is less than 250°F, with the fuel sulfur  
10           content a maximum of 0.05 wt% (preferably less), and a combustion improving amount of dimethyl carbonate.

Example 138

15           The example of 137, wherein the aviation gasoline composition is unleaded and comprises a blend of hydrocarbons, a combustion improving amount of CMT ranging from 0.001 to 1.00 gr. Mn/gal, 0.001 to 5.0 gr. Mn/gal, 0.001 to 0.25 gr. mn/gal, 0.001 to 0.125 gr mn/gal (and amounts greater than 0.25 gr mn/gal), a combustion  
20           improving amount of DMC ranging from 0.01% to 20.0% O2 by weight, whereby the octane rating number as determined by ASTM D 2700 is 100, with the balance of the fuel's specifications conform to strict ASTM standards.

25           Example 139

          The unleaded composition of 137, wherein CMT is greater than 1/16, 1/8/, 1/4, 1/2, or 5/8 gram Mn/gal, and the combustion improving amount of DMC is greater than 1.0%



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O<sub>2</sub> by weight, preferably greater than 1.5%, and the minimum net heat of combustion of composition is approximately 18,500 BTU/lb, 18,720, 18,800 BTU/lb., or more preferably greater than 19,000 BTU/lb.

5

Example 140

The unleaded composition of 137, wherein CMT is greater than 1/16, 1/8, 1/4, 1/2, or 5/8 gram Mn/gal, and the combustion improving amount of DMC is greater than 1.0% O<sub>2</sub> by weight, preferably greater than 1.5%, and the net heat of combustion is approximately 16,500 to 18,500 BTU/lb, wherein flight range is increased at least 5% over the clear fuel.

15

Example 141

A method of operating a aviation gasoline power aircraft; said method characterized: by mixing a fuel of example 137, supplying said fuel to an injection or vaporization system, wherein said fuel is injected into an engine manifold or combustion chamber, wherein average fuel droplet particles is less than 60 microns; whereby combustion of said fuel results in an increase in power, thermal or combustion efficiency of 2.0% or more.

25

Example 142

The method of 141, wherein the fuel is constructed employing DMC such that combustion temperatures are reduced by at least 25°F, and whereby thermal efficiency is improved

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by 5% to 10% and/or the operation of aviation gasoline engine life is extended by at least 5.0%

Example 143

5           The example of 147-140, wherein the fuel additionally has an end boiling temperature of less than 300°F, (or alternatively a T-90 temperature less than 250°F, and/or an average latent heat of vaporization increased of the base fuel of at least 2.0%, preferably 5.0%, or more.

10

Example 144

          The examples of 144, wherein the fuel additionally contains a combustion improving amount of CMT, representing from 1/64, 1/32, 1/16, 1/8, 1/4, 3/8, 1/2, 5/8, 3/4, 1 gr. Mn/gal (with a preferred concentrations greater than 1/4 gram Mn) of the fuel composition.

15

Example 145

          The examples of 137-145, wherein the fuel is non-leaded.

20

Example 146

          The examples of 137-146, wherein the fuel's aromatic content is less than 20 volume percent, and wherein benzene is less than 1.0% by volume.

25

Example 147

          The examples of 141-142, wherein the fuel is combusted in a spark ignited internal combustion engine, equipped

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with fuel injection or manifold, and/or other means, wherein fuel particles averaging 70 microns, or less, are communicated/injected into the combustion chamber; and wherein said combustion is occurring at an altitude of at  
5 5,000 to 10,000 feet above sea level, or more; and wherein combustion efficiency is increased by at least 5.0%.

In the practice of this invention a copper strip corrosion test number of No 1., or less is preferred to avoid corrosion of the metal parts of the fuel system.

10 The maximum freezing point should not exceed  $-72^{\circ}$  F to to preclude solidification of any hydrocarbon components at extremely low temperatures with consequent interference with fuel flow to the engine. It is contemplated that additives, including those specified above, may be employed  
15 to assist in meeting this requirement.

Applicant's aviation gasoline fuels must be usable after storage for variable periods under a variety of climatic conditions. The potential gum test, which is an accelerated oxidation method, is used to estimate fuel  
20 stability in storage and the effectiveness of oxidation inhibitors. If the fuel is to be stored under relatively mild conditions for short periods, an oxidation period of 5 h with a result of no more than 6.0 mg/100 ml employing ASTM D 873 is preferred and contemplated.

25 Whereas a 16-h period, with the same or better results, is desirable to provide stability assurance for long periods and severe conditions such as storage in tropical climates.

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Antioxidants of the type set for above may be used in the practice of this invention to prevent the formation of gum in fuel during storage. The efficacy of a given inhibitor determined by the apparent oxidation stability of a fuel does not completely establish its suitability for use in a gasoline aircraft engine. Oxidation inhibitors have been found to contribute to excessive induction system deposits; therefore, their acceptability for use must ultimately be determined in the full-scale aircraft engine.

Non-limiting inhibitors and the maximum quantities permitted are shown shown in ASTM D 910 specification.

Low boiling aromatics, which are common constituents of aviation gasolines, are known to affect elastomers to a greater extent than other components in aviation gasoline. Thus, it is preferred, as in the case of other fuels, to limit aromatic content. Fortunately, benzene is virtually excluded by the maximum freezing point of  $-72^{\circ}\text{F}$  ( $-58^{\circ}\text{C}$ ), while other aromatics are limited by the minimum heating value and the maximum distillation end point. Thus, the heating value limits toluene to about 24 %. Xylenes have a slightly higher heating value and, therefore, would permit somewhat higher aromatic concentration; however, their boiling points (above  $280^{\circ}\text{F}$  or  $138^{\circ}\text{C}$ ) limit their inclusion at levels not higher than 10%. However, it is still preferred practice to limit aromatic levels to less than 25 % by volume, 20% or less, being more preferred.

Example 148

The aviation gasolines of the above examples meeting ASTM D 910 specifications, and a combustion improving amount of dimethyl carbonate and CMT in a concentration  
5 from about 0.001 grams to about 0.125 grs per gallon.

Example 149

In combination an aviation gasoline meeting ASTM D 910 specifications, a spark ignited aviation gasoline engine,  
10 wherein said combination is characterized in that: said fuel contains a combustion improving amount of dimethyl carbonate and a least one CMT compound in a concentration from about 0.001 grams to about 1.00 grs Mn/per gallon, wherein the combustion of said fuel results in an improved  
15 engine thermal efficiency of 2.0%, or more.

Fuel Oils

The invention contemplates the use of a wide spectrum of fuel oils, as co-fuels and as resultant fuels, including  
20 burner fuels, fuel oils, furnace oils, petroleum and petroleum oils, and those fuel oils meeting ASTM D 396 standards, and/or fuel intended for use in various types of fuel-oil-burning equipment, under various climatic and operating conditions. Non-limiting examples, include ASTM  
25 Grades 1 through 5.

Intended application of combustion systems using Applicant's fuel oils include direct and indirect heat transfers systems, including heaters, superheaters,

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boilers, vaporizers, reformers, dryers, kilns, roasters, incinerators, and heat transfers.

Due to the methods employed in their production, fuel oils fall into two broad classifications: distillates and residuals. The distillates consist of overhead or distilled fractions. The residuals are bottoms remaining from the distillation, or blends of these bottoms with distillates. In this specification, Grades No. 1 and No. 2 are distillates and the grades from No. 4 to No. 6 are usually residual, although some heavy distillates can be sold as Grade No. 4.

Grade No. 1 is a light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.

Grade No. 2 is a heavier distillate than Grade No. 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual fuels.

Grade No. 4 (Light) is a heavy distillate fuel or distillate/residual fuel blend meeting the specification viscosity range. It is intended for use both in pressure-atomizing commercial-industrial burners not requiring

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higher cost distillates and in burners equipped to atomize oils of higher viscosity. Its permissible viscosity range allows it to be pumped and atomized at relatively low-storage temperatures.

5           Grade No. 4 is usually a heavy distillate/residual fuel blend but can be a heavy distillate fuel meeting the specification viscosity range. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible  
10 viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather it requires no preheating for handling.

          Grade No. 5 (Light) is residual fuel of intermediate  
15 viscosity for burners capable of handling fuel more viscous than Grade No. 4 without preheating. Preheating can be necessary in some types of equipment for burning and in colder climates for handling.

          Grade No. 5 (Heavy) is a residual fuel more viscous  
20 than Grade No. 5 (Light) and is intended for use in similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

          Grade No. 6, sometimes referred to as Bunker C, is a  
25 high-viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing. The extra equipment and maintenance

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required to handle this fuel usually preclude its use in small installations.

The invention contemplates a wide range of residual fuel oils having various sulfur contents. It is contemplated that Applicant's fuel oils will meet minimal legal sulfur regulations. In any event, low sulfur fuels are more preferred, especially those with 0.50% mass, or lower. ASTM Test Method D 1266 can be used for Grade 1, but only with samples having sulfur contents of 0.4 mass per cent and less (down to 0.01 %). Applicant appreciates his preferred low sulfur content will often be impractical, but is nonetheless preferred. Obviously, higher sulfur concentrations are acceptable, especially since the corrosive and other deleterious attributes of sulfur are substantially mitigated in the accelerated burning velocity and reduced combustion temperatures of Applicant's invention.

Applicant's fuels will also vary in viscosity. It is preferred that the minimum kinetic viscosity be 1.3, 1.9, 1.9, and less than 5.5 ( $\text{mm}^2/\text{s}$ ) measured at 40°C for Grades No. 1, No. 2, No. 4 (light), and No. 4, respectively. Their preferred maximum viscosity is 2.1, 3.4, 5.5, and 24.0, respectively. Viscosity limits for No. 1 and No. 2 grades are specified to help maintain uniform fuel flow in appliances with gravity flow, and to provide satisfactory atomization and constant flow rate through the small nozzles of household burners.



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Similarly, it is preferred that the minimum kinetic viscosity be 5.0, 9.0, and 15.0 (mm<sup>3</sup>/s) measured at 100°C for Grades No. 5 (light), No. 5 (heavy), and No. 6, respectively. Their preferred maximum viscosity is 8.9, 14.9, and 50.0, respectively. For the heavier grades of industrial and bunker fuel oils, viscosity is of major importance, so that adequate preheating facilities can be provided to permit them to be pumped to the burner and to provide good atomization. However, it is equally important that the maximum viscosity under the existing conditions be such that the oil can be pumped satisfactorily from the storage tank to the preheater.

In the practice of Applicant's invention, his fuel oils should be homogeneous hydrocarbon oils, free from inorganic acid, and free from excessive amounts of solid or fibrous foreign matter.

The resultant fuel oils of the various grades above should generally conform to Table 10. Modifications which improve combustion are, however, expressly contemplated.

In the practice of Applicant's invention, it is preferred that the minimum flash point for Grades No 1., No. 2, No. 4 (light), No. 4, No. 5 (light), No. 5 heavy, No. 6 be 38°C, 38°C, 38°C, 55°C, 55°C, 55°C, 60°C, respectively. However, lower flash points are expressly contemplated.

Applicant's Pour Point practice with fuel oils is similar to his other heavier fuels. It is preferred that the pour point temperatures of Grades No. 1, No 2., No. 4

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(light), and No. 4, be no greater than  $-18^{\circ}\text{C}$ ,  $-6^{\circ}\text{C}$ ,  $-6^{\circ}\text{C}$ , and  $-6^{\circ}\text{C}$ , respectively.

5 It is preferred that Applicant's fuel oils be free, to the extent possible, of water and sediment, to avoid trouble with burner mechanisms, flow obstruction, and corrosion. Applicant's gas turbine fuel practices are contemplated to deal with similar problems of fuel oils storage and/or handling, if necessary.

10 It is preferred that Applicant's carbon residue employing ASTM D 524 methodology not exceed 0.15% mass for No. 1 fuel oils, or 0.35% mass for No. 2 fuel oils, in order to avoid fuel causing deposits in vaporizing burners, such as pot-type and sleeve-type burners, where the fuel is vaporized in an air-deficient atmosphere.

15 It is preferred that the ash content as measured by ASTM D 482 not exceed 0.05, 0.10, 0.15 % max., for Grade No. 4

TABLE 10  
ASTM D 396  
DETAILED REQUIREMENTS FOR FUEL OILS<sup>a</sup>

Property	ASTM Test Method <sup>b</sup>	No. 1	No. 2	Grade No. 4 (Light)	No. 4	No. 5 (Light)	No. (Heavy)	No. 6
Flash Point °C, min.	D 93	38	38	38	55	55	55	60
Water and sediment, % vol. max	D 1796	0.05	0.05	(0.50) <sup>c</sup>	(0.50) <sup>c</sup>	(1.00) <sup>c</sup>	(1.00) <sup>c</sup>	(2.00) <sup>c</sup>
Distillation temperature °C	D 86	215	...	...	...	...	...	...
10 % vol recovered, max		...	282	...	...	...	...	...
90 % vol recovered, min		288	338	...	...	...	...	...
max								
Kinematic viscosity at 40°C, mm <sup>2</sup> /s	D 445	1.3	1.9	1.9	>5.5	...	...	...
min		2.1	3.4	5.5	24.0 <sup>p</sup>	...	...	...
max								
Kinematic viscosity at 100°C, mm <sup>2</sup> /s		...	...	...	...	5.0	9.0	15.0
min		...	...	...	...	8.9 <sup>p</sup>	14.9 <sup>p</sup>	50.0 <sup>p</sup>
max		0.15	0.35	...	...	...	...	...
Ramsbottom carbon residue on 10% distillation residue % mass, max	D 524	...	...	0.05	0.10	0.15	0.15	...
Ash, % mass, max	D 482	...	...	...	...	...	...	...
Sulfur, % mass max <sup>f</sup>	D 129	0.50	0.50	...	...	...	...	...
Copper strip corrosion rating, max, 3 h at 50°C	D 130	No. 3	No. 3	...	...	...	...	...

TABLE 10  
(continued)  
ASTM D 396

DETAILED REQUIREMENTS FOR FUEL OILS<sup>A</sup>

Property	ASTM Test Method <sup>B</sup>	No. 1	No. 2	Grade No. 4 (Light)	No. 4	No. 5 (Light)	No. (Heavy)	No. 6
Density at 15°C, kg/m <sup>3</sup>	D 1298	...	...	>876 <sup>F</sup>	...	...	...	...
min		...	...	...	...	...	...	...
max		850	876	...	...	...	...	...
Pour Point °C, max <sup>G</sup>	D 97	-18	-6	-6	-6	...	...	<sup>H</sup>

<sup>A</sup> It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. However, to meet special operating conditions modifications of individual limiting requirements may be agreed upon among the purchaser, seller and manufacturer.

<sup>B</sup> The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Section 2 and 5.1.

<sup>C</sup> The amount of water by distillation by Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 mass %, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass %.

<sup>D</sup> Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 can be supplied by agreement between the purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

<sup>E</sup> Other sulfur limits may apply in selected areas in the United States and in other countries.

<sup>F</sup> This limit assures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

<sup>G</sup> Lower or higher pour points can be specified whenever required by conditions of storage or use. When a pour point less than -18°C is specified, the minimum viscosity at 40°C for grade No. 2 shall be 1.7 mm<sup>2</sup>/s and the minimum 90 % recovered temperature shall be waived.

<sup>H</sup> Where low sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as Low Pour (+15°C max) or High Pour (no max). Low Pour fuel oil should be used unless tanks and lines are heated.

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(light), No. 4., No. 5 (light), and No. 5 (heavy), respectively, in order to reduce high wear of burner pumps, valves, and deposits on boiler heating surfaces. The lower combustion temperatures of Applicant's invention helps to  
5 reduce ash formation to a certain extent.

Boiling point modification of fuels oils is an express embodiment of this invention. It is expressly contemplated that T-90 temperatures be reduced where practical, but not below minimum required specification temperatures. For  
10 example T-90 temperatures may be reduced 20° C below max ASTM specification temperatures. Reductions of 50° C are also preferred so long as, as in the case of Grade No. 2 fuel oils, T-90 is not reduced below 282° C. There is generally no limit on T-10 or T-50 reductions, nor T-90  
15 reduction (except for No. 2 fuels) so long as the fuel is easily vaporized and operates efficiently, particularly in vaporizing type burners.

A minimum T-90 temperature limitation for Grade No. 2 heating oil is intended to maintain compatibility with  
20 atomizing type household heating burner applications. Otherwise, distillation limits are not specified for fuel oils of Grade Nos. 4, 5, and 6, and T-90 temperatures may be reduced to the extent practical, in order to improve combustion and/or reduce pollutants.

25

Example 150

A No. 2 fuel oil, with a kinetic velocity of no less than 1.9 nor greater than 3.4 (mm<sup>2</sup>/s) measured at 40°C, a

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minimum T-90 temperature of 282°C, a max T-90 temperature of 338°C, a maximum sulfur content of 0.05% mass, a maximum copper strip rating of No.3, a combustion improving amount of an ECS compound.

5

Example 151

A No. 6 fuel oil, with a kinetic velocity of no less than 15.0 nor greater than 50.0 (mm<sup>3</sup>/s) measured at 100°C using ASTM D 445, and combustion improving amount of an ECS compound.

10

Example 152

The example of 150-151, wherein end boiling point and/or T-90 fraction temperatures are reduced at least 30°C, employing boiling point modification.

15

Example 153

The examples of 150-152, wherein an ECS compound, preferably dimethyl carbonate, is added in concentration ranging from 0.01 to 30% oxygen weight percent of fuel.

20

Example 154

The example of 150-151, wherein the fuel contains a combustion improving amount of CMT.

25

Example 155

The example of 151-153, wherein the fuels average latent heat of vaporization is at least 0.5% to 1.5%

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greater than prior to boiling point modification and/or the addition of the ECS component.

Applicant note nitrogen oxide emission regulations have been imposed on certain combustion facilities as a function of fuel nitrogen content. For purposes of these regulations, distillate fuels, low nitrogen residual fuels, and high nitrogen residual fuels have been defined by their nitrogen content. Installations are required to meet different emission standards according to the classification of the fuel being used. When regulations require such a distinction to be made, fuel nitrogen specifications can be needed in the contractual agreement between the purchaser and the supplier.

In the practice of Applicant's invention, for the reasons set forth above, NOx emissions can be greatly reduced, on the order of 1.0%, 2.0%, 5.0%, 8.0%, 10.0% (and often more), absent significant fuel modifications. In fuel oil practice this is a significant achievement.

In Applicant's fuel oil practice, combustion efficiency, as percent of carbon in the fuel burned to CO<sub>2</sub>, is appreciably higher than non-adjusted fuels. For example, expected combustion efficiency increases will range from 1.0% to 15%, with 2.0% to 10% common.

Due to the nature of Applicant's fuel oil chemistry, it preferred that the furnaces employed, of example, have adequate residence time or heat release rates. Preferred burners include higher performance burners having complete

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flame envelopes with heat release rates of 10,000,000 BTU/ft<sup>3</sup>-hr.

It is contemplated that burners will have an acceptable swirl numbers, which are a qualitative indication of turbulence. Alternatively, good pressure drop of the air supply from a window box to a furnace, through a burner is an acceptable means to measure turbulence, etc.

Thus, in the application of this invention it is preferred that a burner have a pressure drop in the range of 10 to 30 inches H<sup>2</sup>O. Higher pressure drops are also acceptable.

As noted, atomization is a preferred practice of this invention.

#### 15     Example 156

A high performance burner with a turndown ratio of 3:1, or higher, a fuel atomization means, which may be mechanical, steam, or compressed air, wherein said atomization occurs under pressure of up to 900 psi (lower pressures are also contemplated).

#### 20     Example 157

The higher performance burner of example 156, having complete flame envelopes with heat release rates of 10,000,000 BTU/ft<sup>3</sup>-hr.



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Example 158

The example of 156-157, wherein the burner is a high swirl burner which is not designed for more than 50% excess air.

5

Example 159

The example 156-157, wherein the burner is a low swirl high excess air burner.

10

Example 160

The burners of examples 156-159, wherein said burner has a pressure drop in the range of 10 to 30 inches H<sup>2</sup>O, or more.

15

Example 161

The examples of 156-159, wherein combustion occurs in such a fashion that secondary air mixes with products of combustion after the combustion envelope has been completed.

20

Example 162

The operation of a furnace containing the ECS based No. 6 fuel, including examples 156-159 above, wherein resultant combustion particulates of unburned carbon are

0.11b/10<sup>6</sup> Btu, or less.

25

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Example 163

The operation of example 159-162 burners in a furnace, employing an ASTM grade fuel oil, containing a combustion improving amount of dimethyl carbonate and a combustion improving metallic, wherein expected combustion efficiency of the furnace increases in range of at least 1.0% to 20%.

Applicant notes his invention also contemplates the fuilidized combustion of coal. For example, combustors employing minus 10 mesh coal experience similar reductions in pollutants and improved combustion efficiencies.

Likewise, in the case of heavy diesel, locomotive and marine applications, this invention has particular significance. For example it is contemplated that his locomotive and marine fuels will meet appropriate ISO DIS 8217 and BS MA 100 standards. And, because of the sulfur content of locomotive and marine fuels is often higher than most fuels, Applicants invention due to its combustion temperature object, tending to mitigate sulfur corrosion and other pollutants, is particularly attractive.

Example 164

A method of operating a heavy diesel, locomotive or marine fuel composition, wherein the method comprises mixing a fuel meeting ISO DIS 8217 and BS MA 100 standards and wherein said fuel contains a sulfur concentration of 0.01 to 3.0% mass (amounts less than 0.05% are acceptable), a viscosity of 10 to 500 centistokes at 50°C applications; and additionally contains an ECS fuel; whereby combustion

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of resultant fuel in said heavy diesel, locomotive or marine engine results in reduced corrosion and improved fuel consumption of at least 1.0% or more.

5     Example 164a

      The method of 164, wherein said operation of said heavy diesel, locomotive or marine engine is under moderate to high load conditions; whereby fuel consumption is improved by at least 0.5% to 5.0%, or more, over fuel  
10   absent ECS fuel.

Example 165

      The fuel composition of example 164, additionally contains an ashless dispersant, which may be selected from  
15   an alkenyl succinic acid esters, alkenyl succinimide of an amine, methylamine, 2-ethylhexylamine, n-dodecylamine, and the like (see U.S. Patents 3,172,892; 3,202,678, 3,219,666, 4,234,435).

20   Example 166

      The above fuel compositions, wherein the fuel contains an antioxidant.

Example 167

25   The fuel composition of example 164-165, wherein the ECS fuel contains dimethyl carbonate from 0.01 to about 30.0% volume and a combustion improving amount of CMT.

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Example 168

A method of improving thermal efficiency in the operation of a locomotive or marine engine, wherein said method comprises: injecting an ECS based heavy fuel composition into a combustion chamber, wherein combustion occurs at an accelerated, more efficient rate, and combustion temperatures are reduced; whereby thermal efficiency increased by at least 5%.

10 Rocket Fuel Applications

Rocket engine propulsion is a particularly desirable object of this invention.

Applicant's rocket engine application, which converts fuel energy into suitable form and ejects stored matter via an engine to derive momentum, makes Applicant's invention especially desirable, particularly due its reduced combustion temperatures and supersonic expansion capabilities.

An object of Applicant's rocket fuel application is to deliver high impulse, high thrust/power at reduced combustion temperatures, which is a significant and material departure from the prior art. Such object will be translated in increased engine life, smaller combustion chambers, lighter weight construction (avoiding certain cooling features), and the like.

Thus, it is a specific embodiment that Applicant's liquid rockets be able to maintain the same essential

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impulse and thrust characteristics, while minimizing weight without sacrificing reliability.

5 A particularly desirable object of instant invention is the ability to achieve near thrust/power performance formerly only associated with compressed liquids, namely hydrogen and oxygen. Applicant's invention is able to achieve similar results employing liquid fuels or hybrids, absent the disability of special storage, cryogenics, liquidification, handling and the like.

10 A wide range of rocket systems are contemplated. Liquid, gaseous, and solid propellant systems, and mixture, hypergolic and non-hypergolic are contemplated.

15 Non-limiting solid rockets propellants include double base or colloidal, cordite or extruded double base, composite, pressed, plastic, propellants with polymerized binders, composite modified double base, molecular, and the like.

20 Applicant's invention contemplates a polymeric binder system which serves to hold the propellant together, the major portion being a crystalline oxidizer, and optionally a metallic fuel additive for increases specific pulse and density. Applicants double base composites, in which a nitro-glycerine-nitrocellulose is used as a binder with an inorganic binder and metallic additives. The common polymer  
25 types, unmetallized solid propellants and metallized solid propellants are known in the art.

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In the practice of solid fuels, Applicant's solid ECS compounds will be employed, and/or the use of a hybrid liquid/solid system may be employed.

5 The rocket engine propulsion systems of Applicant's invention include rocket and ducted rocket propulsion. Ram jet and air augmented rockets are also contemplated.

10 The contemplated liquid propellants include bi-propellant (fuel and oxidizer), mono-propellant, gaseous propellants, and hybrid propellants. Examples of liquid rocket propellant engines of Applicant's invention include NASA's manned and unmanned Saturn, Atlas, and Titan programs. The rockets contemplated in this invention include those designed for spacecraft propulsion, booster propulsion, air launched missile, ballistic missile, anti-  
15 air craft missile, jet assisted take off, catapult acceleration, aircraft power plant, attitude control, interplanetary vehicle propulsion, submarine launched missiles, and anti-ballistic devices.

20 The rocket engine propulsion systems of Applicant's invention include rocket and ducted rocket propulsion. Ram jet, scram jet, and air augmented rockets are also contemplated.

#### Example 169

25 A liquid bipropellant and monopropellant rocket engine with a pressure fed system used in low thrust or high thrust vehicle attitude control and/or maneuvering

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applications employing an efficient pulse performing engine and rocket fuel.

Example 170

5           The example of 169, wherein said pulse performance is extremely efficient for very short durations of 0.020 seconds or less.

Example 171

10           The examples of 169-170, wherein said pulse performance system must be restarted at least 1,000 times or more, per flight mission.

Example 172

15           The example of 169, wherein the pulse control engine has a thrust of 20.0 lb., employs an ablative thrust chamber, wherein system experiences at least 2,000 restarts, a total accumulative duration of at least 600 seconds pulse operation, and a minimum mission period of  
20           one week.

Example 173

          The example 169, wherein the engine is an aerospike engine.

25           One of the attractive objects of Applicant invention is the reduction of combustion temperatures, which in the normal application of liquid propellant engines can range from 4,000°F to 7,000°F.

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Appreciable reductions of combustion temperatures permit improved design and opportunities to increase thrust, and usage of thrust improving metallics, like boron, lithium, manganese, aluminum, beryllium, trimethylaluminum, dimethylberyllium, and the like.

Acceptable oxidizers in the practice of this invention include liquid oxygen, nitric acid, mixed nitric acid sulfuric acid combinations, fluorine, chlorine trifluoride, perchloryl fluoride, nitrosyl fluoride, nitryl fluoride, nitrogen trifluoride, difluorine monoxide, fluorate, chlorine oxides, nitrogen tetroxide, hydrogen peroxide, potassium perchlorate, perchloryl fluoride, bromine pentafluoride, chlorine trifluoride, ON 7030, ozone, oxygen difluoride, RFNA (at various strengths), WFNA, tetranitromethane and the like.

In the practice of this invention ECS compounds may be used in combination with themselves as mixture, and/or in combination with propellant fuels. Non-limiting examples of contemplated propellant or co-propellant fuels include acetylene, aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, diborane, dimethylamine, diethylenetriamine, dicyanogen, ethane, ethanol, ethylamine, ethylene, ethylene diamine, ethylene oxide, ethylenediamine, ethyl nitrate, dimethyl sulfide, furfuryl alcohol, gasoline, heptene, hydrazine (including substituted hydrazines), hydrogen, isoethyl nitrate, isopropyl alcohol, JP-3, JP-4, kerosene, lithium, lithium hydride, methane, methylal, methanol, methyl nitrate,



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methylaniline, methylacetylene, methylvinyl acetylene, monoethylaniline, nitromethane, nitropropane, nitroglycerine, n-octane, propane, propylene oxide, n-propyl nitrate, o-toluidine, triethylamine, trimethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, xylidine, 2,3-xylidine, lithium borohydride, monomethylhydrazine, pentaborane, and the like. Metallic propellants are also contemplated including trimethylaluminum and dimethylberyllium.

10

Example 173a

A method of operating a rocket, wherein an ECS fuel (e.g. ECS compound and metallic) is employed, and optionally with at least one oxidizer and/or rocket co-fuel; combusting said fuel in said engine; whereby engine temperatures are reduced 100°F to 1000°F; such that thrust is increased and/or engine weight can be reduced.

15

Example 173b

The method of 173a, wherein combustion wall temperatures are controlled and do not exceed 1,300°F to 2,000°F.

20

Example 174

A rocket propellant comprising DMC, and optionally an oxidant; (including those set forth above, desirably being nitric acid (HNO<sub>3</sub>) and/or hydrogen peroxide); and a metallic.

25

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Example 175

The example of 174, wherein the propellant contains a co-fuel selected from the group set forth above.

5      Example 176

The example of 174, wherein the oxidizer is N2O4.

Example 177

10      A method employing the rocket fuels of examples 169-172, wherein specific pulse thrust is enhanced absent combustion temperature increases.

15      It is thus an embodiment to operate Applicant's monopropellant fuels, especially those based on hydrogen peroxide or hydrazine, together with aforementioned metallic, such that combustion wall temperatures not exceed 1,300°F and 2,000°F, respectively. Similar wall temperatures are expected from monopropellant use of dimethyl carbonate, and/or alternative multiple fuel propellant (one including DMC), and/or one oxidant and/or multiple oxidant.

20      It is thus a further embodiment to improve rocket engine design to reduce total weight as a consequence of Applicant's methods for controlling combustion temperature, so that increased amounts of high heat releasing metallic(s) and/or other propellants may be employed. This  
25      unexpectedly permits a means to increase specific impulse or thrust, absent additional weight costs.

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Example 178

A method of increasing specific impulse power of a rocket engine, absent attendant increases in combustion temperatures, said method comprising: supplying a fuel composition of the nature of examples 173a-177, to a rocket combustion chamber system, wherein explosive combustion occurs, such that by maintaining a combustion chamber pressure of 500 psi, the specific impulse from said combustion is in excess of 200  $I_{sp}$ sec (more preferably greater than 250  $I_{sp}$ sec ).

Example 179

The method of example 178, wherein the fuel is injected into the rocket's combustion chamber, employing an injector selected from the group consisting of impinging fuel-oxider injectors, pre-mix injectors, "built in" variable valve injectors, wherein injector orifices are selected from the group consisting of short tube with rounded entrance, short tube with conical entrance, sharp-edged cone, and sharp-edged orifice.

Improvements in thrust or specific impulse are material representing increases of 3.0% to 15.0% over existing systems. Minimal improvements will be on the order of 1.0% to 3.0% over existing systems and similar fuels. Substantial improvements will be on the order of 10% to 50%.

Reduced combustion temperatures allow improvements in regenerative cooled thrust chambers, which employ one of

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the liquid propellants to circulate through a cooling jacket to absorb heat from the combustion walls.

Other systems of cooling combustion walls, which can be improved with attendant savings in weight, include, radiation-cooled chambers, wherein the thrust chambers are constructed out of refractory; ablative thrust chambers, where the walls are made of special composites which are consumed at a slow rate to essentially form protective boundaries. Yet others include turbine exhaust gas cooling, heat sink cooling, insulation cooling, dump cooling, ablative cooling, regenerative cooling, film cooling, transpiration cooling, and combined methods.

Another advantage of applicant's invention is the ability to improve storability of propellants. Thus, reliable, low-cost liquid storable propellant prepackage applications are contemplated.

Another substantial advantage is the lower costs of producing Applicant's rocket fuels, when compared to costs of existing fuels. Applicant expects to be able to reduce rocket fuel cost as much as 50% below existing rocket fuels.

Applicant notes, that preferred ECS embodiment employing dimethyl carbonate shows DMC's oxygen storage capabilities, representing an excellent oxidizer, as well as a fuel.

Manganese concentrations, if employed, will be significant, ranging from 0.5 grams to 1000 grams per gallon, and greater, as circumstances require. Hypergolic

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concentrations normally exceed 6% weight of the fuel. Maximum concentrations are dictated by the limits of acceptable combustion. CMT also has appears to have some attractive ignition catalyst properties when associated  
5 hydrogen peroxide applications, especially in hypergolic fuels.

In Applicant's rocket applications, when oxidant systems with external source ignitions are employed, ignition is smoother with reduced ignition delays.

In the practice of this invention primary aromatic  
10 amines, such as aniline, xylidine and mixture, are contemplated to reduce ignition delay, especially when nitric acid is employed.

It is the desired practice of Applicant's invention to employ an ECS compound (preferably dimethyl carbonate) as  
15 a propellant with an oxidizer and/or a metallic. Additional co-fuels are also contemplated.

Applicant appreciates that DMC has attributes of a mono-propellant, especially with air-breathing augmentation. It is contemplated that DMC may be employed  
20 solely as fuel requiring addition of an oxidizer, or alternatively serve as an oxidizer with a fuel. In the later circumstance and additional oxidizer or air breathing augmentation may be required.

None-the-less it is an embodiment that DMC with a  
25 metallic to serve as a principal component of the rocket propulsion process.

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Example 180

A rocket fuel propellant comprising an ECS compound selected from the group of dimethyl carbonate, acetylene, aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, diborane, diethylenetriamine, ethane, ethanol, ethylamine, ethylene, ethylene diamine, ethylene oxide, ethyl nitrate, furfuryl alcohol, gasoline, heptene, hydrazine (including substituted hydrazines), hydrogen, isopropyl alcohol, lithium, lithium hydride, methane, methylal, methanol, methylamine, nitromethane, nitropropane, n-octane, propane, n-propyl nitrate, o-toluidine, triethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, 2,3-xylidene, lithium borohydride, monomethylhydrazine, pentaborane, and mixture; and a propulsion improving amount of a metallic.

Example 181

The example of 180, wherein composition additionally comprises a known oxidizer, selected from the group consisting of liquid oxygen, nitric acid, mixed nitric acid sulfuric acid combinations, fluorine, nitrogen tetroxide, hydrogen peroxide, potassium perchlorate, perchloryl fluoride, bromine pentafluoride, chlorine trifluoride, ON 7030, ozone, oxygen difluoride, RFNA (at various strengths), WFNA, tetranitromethane, fluorine, chlorine trifluoride, perchloryl fluoride, nitrosyl fluoride, nitryl fluoride, nitrogen trifluoride, difluorine monoxide, fluorate, chlorine oxides, and the like.

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Example 182

A rocket fuel composition comprising hydrogen peroxide and a metallic, such as cyclopentadienyl manganese tricarbonyl compound, and optionally, DMC.

5

Example 183

A rocket fuel composition comprising hydrogen peroxide, an oxidizer and a metallic, and optionally DMC.

10

Example 184

The rocket fuel composition of 183, wherein the metal is selected from the group consisting of cyclopentadienyl manganese tricarbonyl, technetium, rhenium, aluminum, beryllium or boron compound, including pentaborane, decaborane, barazole, aluminum borohydride, trimethylaluminum, beryllium borohydride, dimethylberyllium, lithium borohydride, homologues thereof, and mixtures.

15

20

Example 185

The example of 183, wherein the oxidizer is selected from the group consisting of liquid oxygen, nitric acid, mixed nitric acid sulfuric acid combinations, fluorine, nitrogen tetroxide, hydrogen peroxide, potassium perchlorate, perchloryl fluoride, bromine pentafluoride, chlorine trifluoride, ON 7030, ozone, oxygen difluoride, RFNA (at various strengths), WFNA, tetranitromethane, and mixture.

25

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Example 186

A rocket fuel composition comprising dimethyl carbonate, hydrazine and a cyclopentadienyl manganese tricarbonyl compound.

5

Example 187

A rocket fuel composition comprising dimethyl carbonate and an oxidizer selected from the group consisting of nitric acid or sulfuric acid, inclusive or exclusive of a metallic.

10

Example 188

A rocket fuel comprising dimethyl carbonate, hydrazine or a substituted hydrazine, and/or hydrogen peroxide, and/or a metallic.

15

Example 189

A rocket fuel comprising dimethyl carbonate, hydrazine, and kerosine; and optionally a metallic.

20

Example 190

A rocket fuel comprising dimethyl carbonate, hydrogen, a metallic and optionally an oxidizer.

25

Example 191

A rocket fuel comprising dimethyl carbonate, salicyl aldehyde and a metallic.



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Example 192

A rocket fuel for air breathing systems comprising dimethyl carbonate, a metallic; and optionally a rocket co-fuel; and optionally an oxidizer.

5

Example 193

Example 5, wherein non-limiting examples of a rocket co-fuel include hydrogen, hydrazine and kerosene.

10 Example 194

A rocket fuel composition comprising hydrogen peroxide, CMT, and a co-propellant selected from the group consisting of dimethyl carbonate, acetylene, aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, 15 diborane, diethylenetriamine, ethane, ethanol, ethylamine, ethylene, ethylene diamine, ethylene oxide, ethyl nitrate, furfuryl alcohol, gasoline, heptene, hydrazine (including substituted hydrazines), hydrogen, isopropyl alcohol, lithium, lithium hydride, methane, methylal, methanol, 20 methylamine, nitromethane, nitropropane, n-octane, propane, n-propyl nitrate, o-toluidine, triethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, 2,3-xylidene, lithium borohydride, monomethylhydrazine, pentaborane, and mixture; and a 25 propulsion improving amount of a cyclomatic manganese tricarbonyl compound.

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Those skilled in the art will appreciate that many variations and modifications of the invention disclosed herein may be made without departing from the spirit and scope thereof.

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Thus having disclosed my invention, I claim:

- 1) A composition of matter comprised exclusively of one or more ECS compound; and a combustion improving amount of at least one fuel soluble metallic compound of high heating value containing at least one compound comprising at least one metal selected from the group consisting of aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium, gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybden, nickel, niobium, phosphorus, potassium, pallium, rubibidium, sodium, tin, zinc, praseodymium, rhenium, salane, vanadium, and mixture; wherein the composition is characterized as having minimum latent of heat of vaporization of 200 btu/lb @ 60°F, or equivalent;
- 2) The composition of claim 1 having a minimum laminar burning velocity of 48 cm/sec.
- 3) The composition of claim 1 additionally contains a majority of a co-fuel selected from the group selected from a recognized alternative fuel, hydrogen, petroleum gas, liquefied petroleum gas, LPG-propane, LPG-butane, natural gas, natural gas liquids, methane, ethane, propane, n-butane, propane-butane mixture, fuel methanol, e.g. M 80, M 90, or M 85 fuels, fuel ethanol, biomass fuels, vegetable oil fuels, automotive gasoline, aviation gasoline fuels, including grade 80, grade 100, grade 10011, conventional automotive gasolines, reformulated gasolines, low vapor

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pressure gasolines, low sulfur gasolines, kerosine, wide range boiling fuels, gas turbine fuels, aviation jet turbine fuels including JP-4, JP-5, JP-7, JP-8, JP-9, JP-10, TS, Jet A-1, Jet A, Jet B, military aviation gasolines, missile fuels, solid and liquid rocket fuels, monopropellant, multipropellant fuels, hypergolic fuels, gas oil turbine-engine fuels, including grades 0-4, stratified-charged engine fuels, diesel fuels, including Grade low sulfur No. 1-D, Grade low sulfur No. 2-D, Grade No. 1-D, Grade No. 2-D, and Grade No 4-D, and older grades Type C-B, Type T-T, Type R-R, Type S-M, reformulated diesel fuels, fuel oils, including Grade 1, Grade 2, Grade 4 (light), Grade 4, Grade 5 (light), Grade 5 (heavy), Grade 6, heavy diesel fuels for marine or railroad, including those complying with ISO DIS 8217 and BS MA 100 standards, various distillate oils, residual type oils, cycle oils, light cycle oils, light cycle gas oils, heavy cycle oils, heating oils, heavy cycle gas oils, vacuum oils, burner oils, furnace oils, coal liquids, SRC-II middle distillate coal fuels, near coal liquids, powdered coal, tar sand fuels, shale oil fuels, hydrazine, ammonia acetylene, and fuels meeting ASTM specifications, EPA certification standards, industry and/or governmental specifications, present and future, including mixtures thereof;

25

4) The composition of claim 3, wherein the co-fuels are wide boiling hydrocarbons, wherein end boiling point and T-

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90 temperatures are been reduced to increase the average latent heat of vaporization of the composition.

5) A method of creating a pre-combustion vapor, said  
5 method comprising: vaporizing or injecting a fuel under suitable pressure into an air breathing combustion system comprised exclusively of at least one ECS compound having latent heat of evaporation exceeding 200 btu/lb @ 60°F, more preferably 300 btu/lb @ 60°F, and laminar burning velocity  
10 exceeding 48 cm/sec; wherein said vapor contains at least one metallic; and where upon injection or vaporization the particle size of said ECS comound and metal is less than 70 microns; introducing sufficient temperature to the vapor to cause ignition whereafter the unburned vapor has decomposed  
15 into a substantial amount of H, CO, OH, free radicals; diffusing said free radicals ahead of the flame front.

6) The method of 5, wherein at least one oxygenated ECS compound is contained in the unvaporized fuel, and wherein  
20 the unvaporized fuel's latent heat of vaporization exceeds 26 kJ mol<sup>-1</sup> at its boiling temperature.

7) The method of 5, wherein the pre-combustion vapor is a product derived from dimethyl carbonate and a cyclomatic  
25 manganese compound.

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8) The method of 5, wherein the pre-combustion vapor is a product derived from dimethyl carbonate and a metal selected from boron, magnesium, manganese, or mixture.

5 9) The method 5, wherein said vapor additionally comprises a vapor derived from a carbonaceous co-fuel, such that said carbonaceous vapor on a mass basis is the majoritarian vapor; whereby combustion burning velocity of resultant vapor is increased by at least 5% and combustion  
10 temperatures are reduced by at least 10<sup>0</sup>F over vapor of the co-fuel only.

10) The method of 5, wherein the co-fuel vapor is derived from an alternative fuel, hydrogen, petroleum gas,  
15 liquefied petroleum gas, LPG-propane, LPG-butane, natural gas, natural gas liquids, methane, ethane, propane, n-butane, propane-butane mixture, fuel methanol, e.g. M 80, M 90, or M 85 fuels, fuel ethanol, biomass fuels, vegetable oil fuels, automotive gasoline, aviation gasoline fuels,  
20 including grade 80, grade 100, grade 100ll, conventional automotive gasolines, reformulated gasolines, low vapor pressure gasolines, low sulfur gasolines, kerosine, wide range boiling fuels, gas turbine fuels, aviation jet turbine fuels including JP-4, JP-5, JP-7, JP-8, JP-9, JP-  
25 10, TS, Jet A-1, Jet A, Jet B, military aviation gasolines, missile fuels, solid and liquid rocket fuels, monopropellant, multipropellant fuels, hypergolic fuels, gas oil turbine-engine fuels, including grades 0-4,

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stratified-charged engine fuels, diesel fuels, including Grade low sulfur No. 1-D, Grade low sulfur No. 2-D, Grade No. 1-D, Grade No. 2-D, and Grade No 4-D, and older grades Type C-B, Type T-T, Type R-R, Type S-M, reformulated diesel fuels, fuel oils, including Grade 1, Grade 2, Grade 4 (light), Grade 4, Grade 5 (light), Grade 5 (heavy), Grade 6, heavy diesel fuels for marine or railroad, including those complying with ISO DIS 8217 and BS MA 100 standards, various distillate oils, residual type oils, cycle oils, light cycle oils, light cycle gas oils, heavy cycle oils, heating oils, heavy cycle gas oils, vacuum oils, burner oils, furnace oils, coal liquids, SRC-II middle distillate coal fuels, near coal liquids, powdered coal, tar sand fuels, shale oil fuels, hydrazine, ammonia acetylene, and fuels meeting ASTM specifications, EPA certification standards, industry and/or governmental specifications, present and future, including mixtures thereof.

11) The method of 5, wherein the vapor additionally comprised a co-fuel vapor; and wherein the combustion of said vapor powers an engine operated under moderate, or greater, load conditions; whereby fuel economy of said operation is 0.5% to 20.0%, greater than co-fuel alone.

12) The method 5, wherein said vapor additionally contains at least one vapor from an engine, carburetor and/or induction/injection system cleaning detergent/dispersant, including commercially available

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long-chain dibasic acid derivatives (e.g. succinimides such as HiTec 4450), long-chain aliphatic polyamines (e.g. polyisobutenyl polyamine), or long chain Mannich bases, and/or an ashless detergents, including a polyether amine, polyalkenyl amine, alkenyl succinimide, polyether amide amine, and mixture, and an antioxidant, demulsifer, emulsifer corrosion inhibitor, aromatic solvent, scavenger, diluent oil, mutual solvent, metal deactivator, and mixture.

10

13) The method of 5, wherein said vapor additionally contains a co-fuel vapor and is combusted in an engine or combustor selected from group consisting of rocket engine, Brayton cycle engine, gas oil turbine, aviation jet turbine, diesel, marine, locomotive, aviation gas engine, automotive engine, oil burner, residue burner, oil furnace, gas burner, gas furnace, internal compression engine, spark-ignited internal combustion engine, lean burn, fast burn, external combustion Stirling or Rankine engine, Otto cycle engine, or catalyst system.

20

14) The method of 5, wherein the vapor additional comprises a an oxidizer.

25

15) The method of claim 5, additionally containing a co-fuel vapor and wherein the latent heat of vaporization of the co-fuel is increased and/or its burning velocity increased, by reducing end boiling point/T-90 temperatures



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and/or controlling T-50 temperatures of liquid co-fuels from which the vapor is derived.

- 5 16) A method of making a conventional or reformulated gasoline composition comprising cutting higher boiling point fuel fractions such that cut clear fuel's average latent heat of vaporization is at least 0.5% and more preferably 1.5%, or higher than the uncut clear fuel.
- 10 17) The method of 16, wherein a up to 1/32 gr Mn/gal of MMT is mixed into the composition, such that there results an increase of the fuel economy of at least 1.0%.
- 15 18) The method of 16, wherein the cut fuel containing metallic is combusted and exhausted through an three-way exhaust catalyst system wherein an OBD-II catalyst monitor is employed; whereby manganese oxide deposition on catalyst wash coat is sufficiently controlled that said catalyst monitor does not fail.
- 20 19) The method of 16, wherein an oxygenated ECS compound is added at 1.1 to 2.7% oxygen by weight to the base fuel, and wherein the resultant T-50 temperature exceeds 170°F but is less than 220°F; and whereby fuel's T-90 temperature
- 25 absent the presence of the oxygenate does not exceed 300°F; and combustion occurs and emissions are exhausted through an exhaust catalyst where an OBD-II catalyst monitor is employed; such that manganese oxide deposition upon

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catalyst wash coat is sufficiently controlled that said monitor does not fail.

20) A method of increasing the fuel economy of a vehicle  
5 operating on convention or reformulated gasoline, said  
method comprising: Reducing the gasoline boiling  
temperature such that its T-90 fraction is no greater than  
270°F; mixing MMT into the composition up to 1/32 gr mn/gal;  
combusting said composition in a gasoline powered vehicle;  
10 whereby fuel economy is improved by 0.5% or more.

21) The method of 20, wherein fuel economy is improved  
over both the clear fuel not having reduced T-90  
temperatures and same fuel containing MMT.  
15

22) A method of increasing the fuel economy of a gasoline  
engine, said method comprising: Cutting a gasoline fraction  
such the boiling temperature of it's T-90 fraction is no  
greater than 270°F; mixing MMT up to 1/32 gr mn/gal in the  
20 composition; combusting said composition in a gasoline  
powered vehicle; whereby fuel economy is improved by 0.5%  
or more.

23) A method of avoiding catalyst exhaust plugging, said  
25 method comprising: mixing an ECS fuel with sufficiently  
high latent heat of vaporization in sufficient quantity  
with a conventional unleaded or reformulated gasoline  
containing 1/32 gr or more Mn/gal of MMT; combusting said

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fuel wherein said fuel's exhaust temperatures are reduced; venting said gases into an exhaust catalyst wherein inlet gas temperature to less than 1400°f; venting gases into the atmosphere.

5

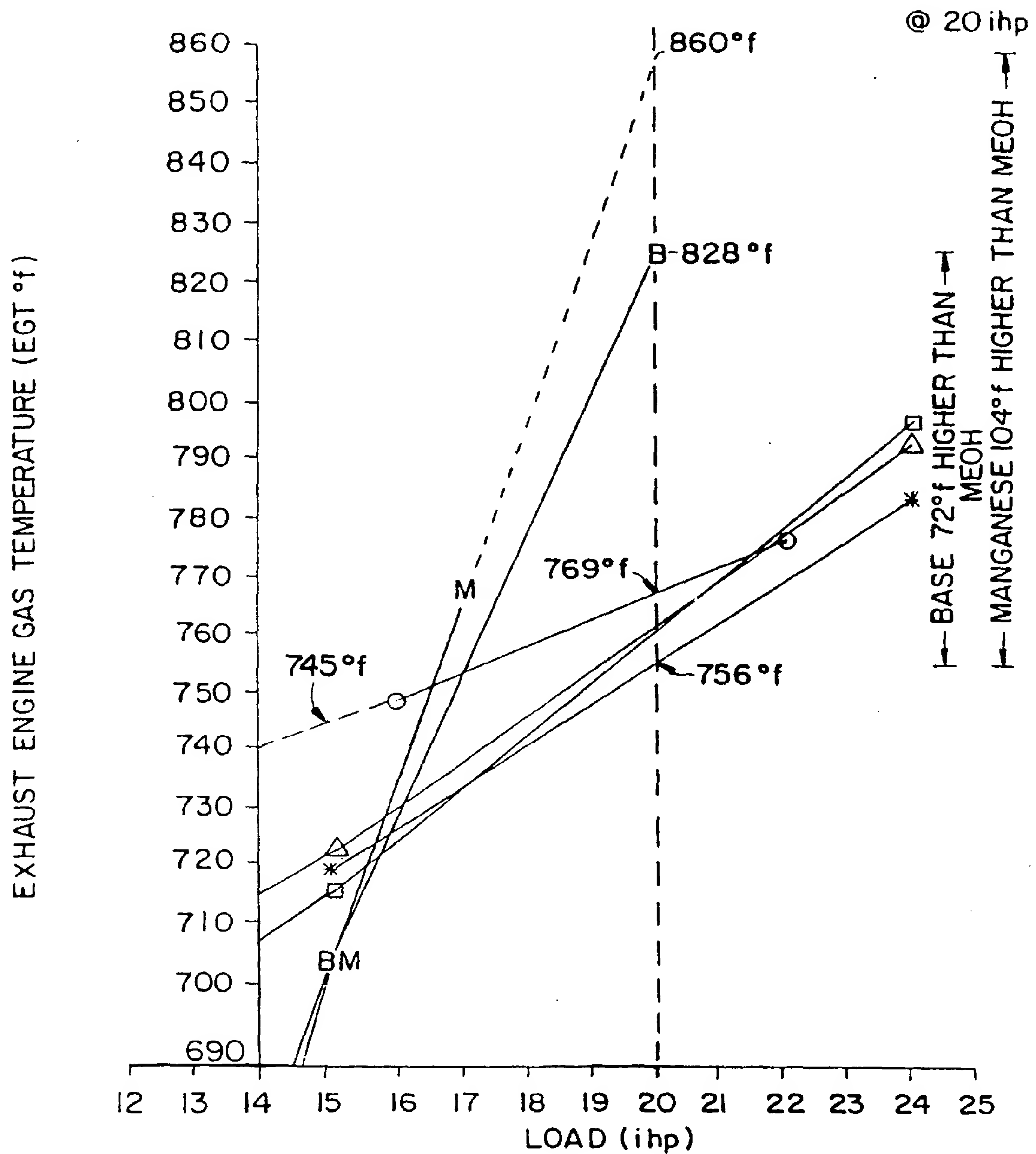
24) A method of operation an internal gasoline combustion engine, said method comprising: mixing a convention, non-convention, or reformulated gasoline with a combustion improving amount of an ECS compound and a combustion improving amount of MMT/and/or other metallic; combusting  
10 said fuel in said engine, wherein engine is under load of at least 12.5 ihp (more preferably 16.0 ihp), wherein fuel economy is increased.

15 25) The method of 24, wherein the load is approximately 20 ihp and fuel economies are improved 5% to 30%.

26) The method of 24, wherein said fuel contains oxygen by weight of 0.05% to 3.7%, supplied by MTBE, ETBE, DMC,  
20 methanol, ethanol, or methylal, or mixture, and 1/64 to 1/4 gram Mn/gal of MMT; and wherein engine is operated at load exceeding 16 ihp; whereby fuel economy is improved.

## 1 / 7 FIG. 1 (TEST TWO)

## COMBUSTION TEMPERATURE DIFFERENCES

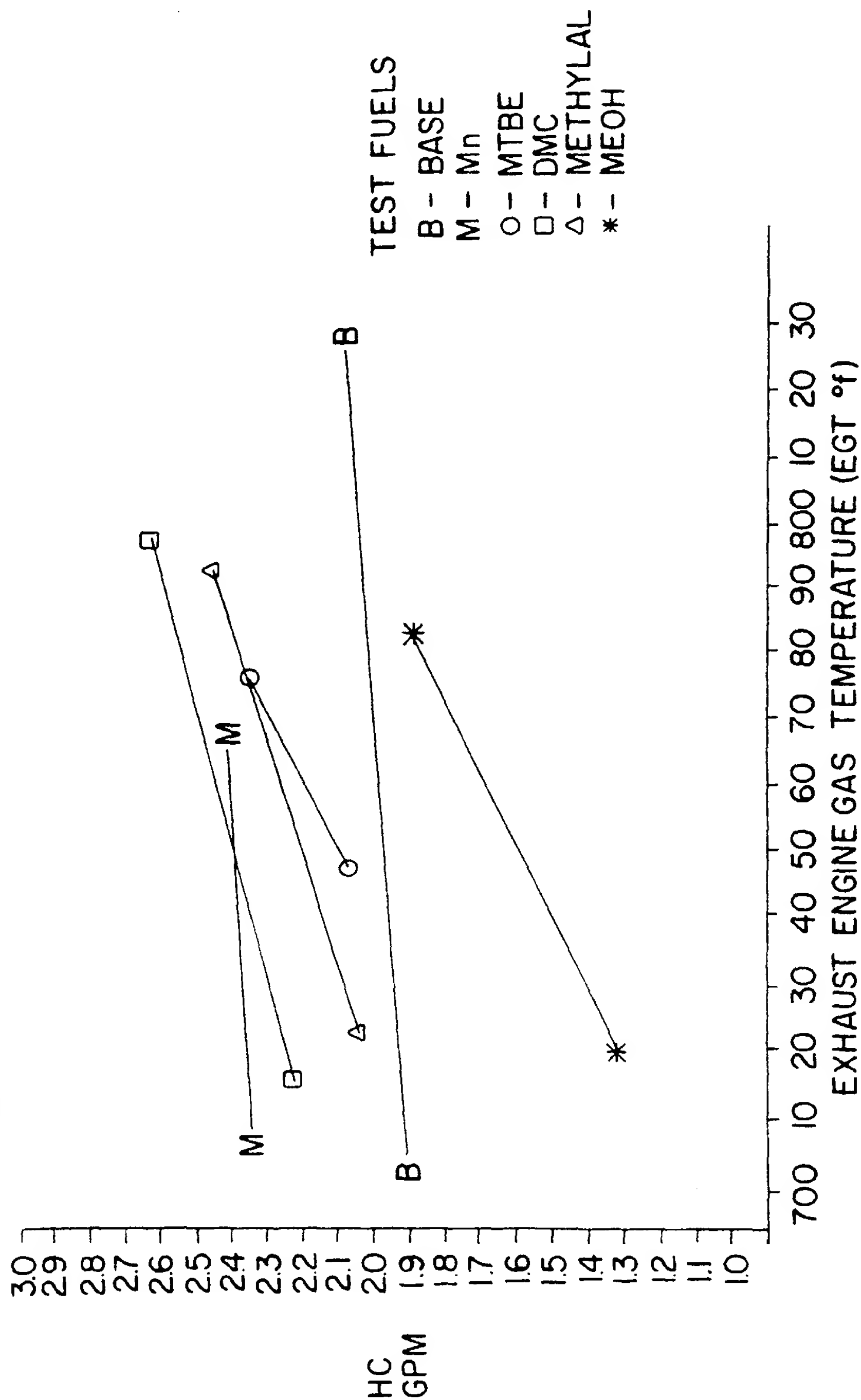


- B - BASE FUEL  
 M - MANGANESE FUEL  
 O - MTBE FUEL  
 □ - DMC FUEL  
 △ - METHYLAL FUEL  
 \* - MEOH FUEL

RECTIFIED SHEET (RULE 91)

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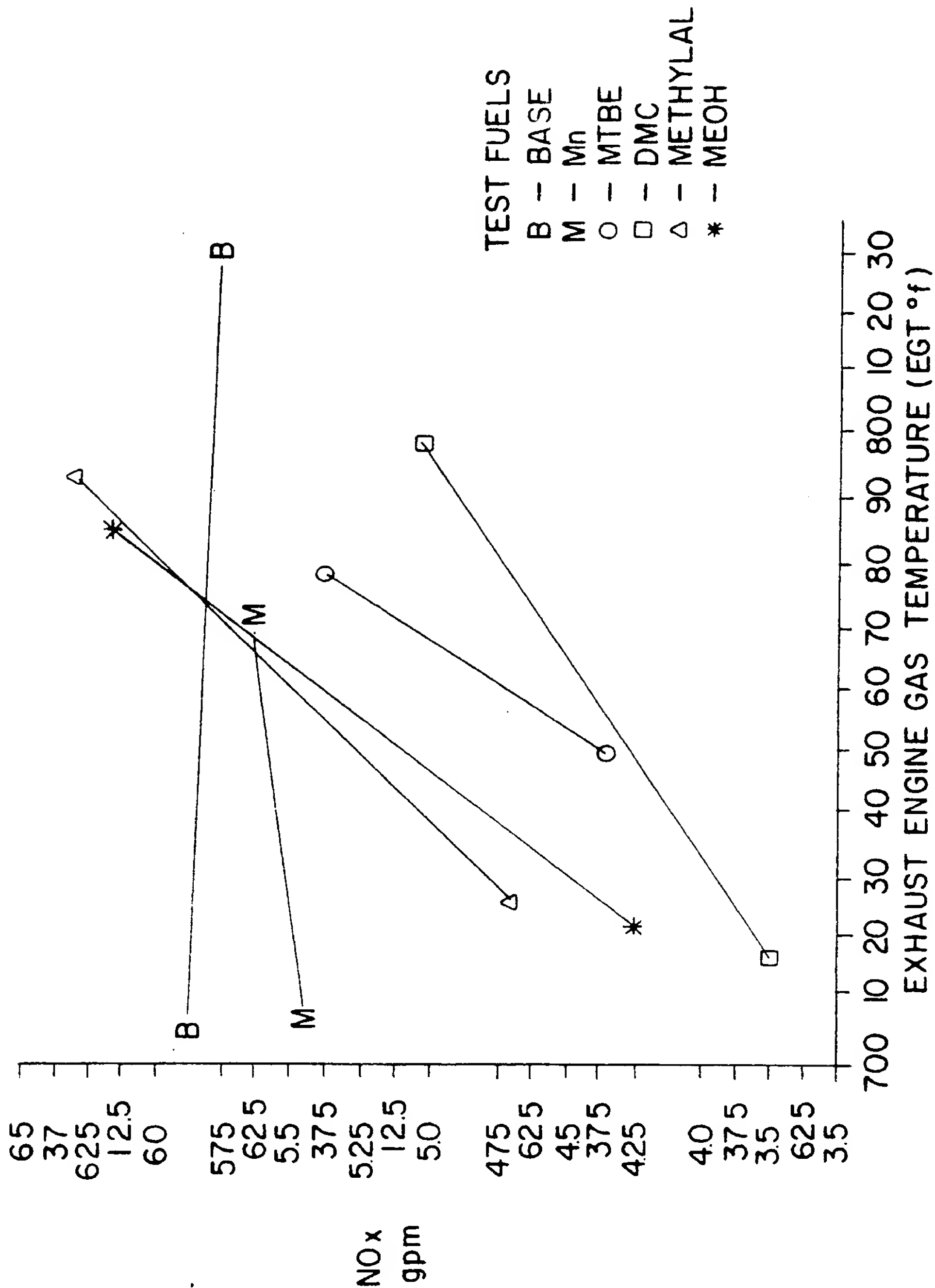
**FIG.2 (TEST TWO)**  
COMBUSTION TEMPERATURES AND HYDROCARBON EMISSIONS



RECTIFIED SHEET (RULE 91)

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**FIG.3 (TEST TWO)**  
COMBUSTION TEMPERATURES AND NO<sub>x</sub> EMISSIONS



RECTIFIED SHEET (RULE 91)

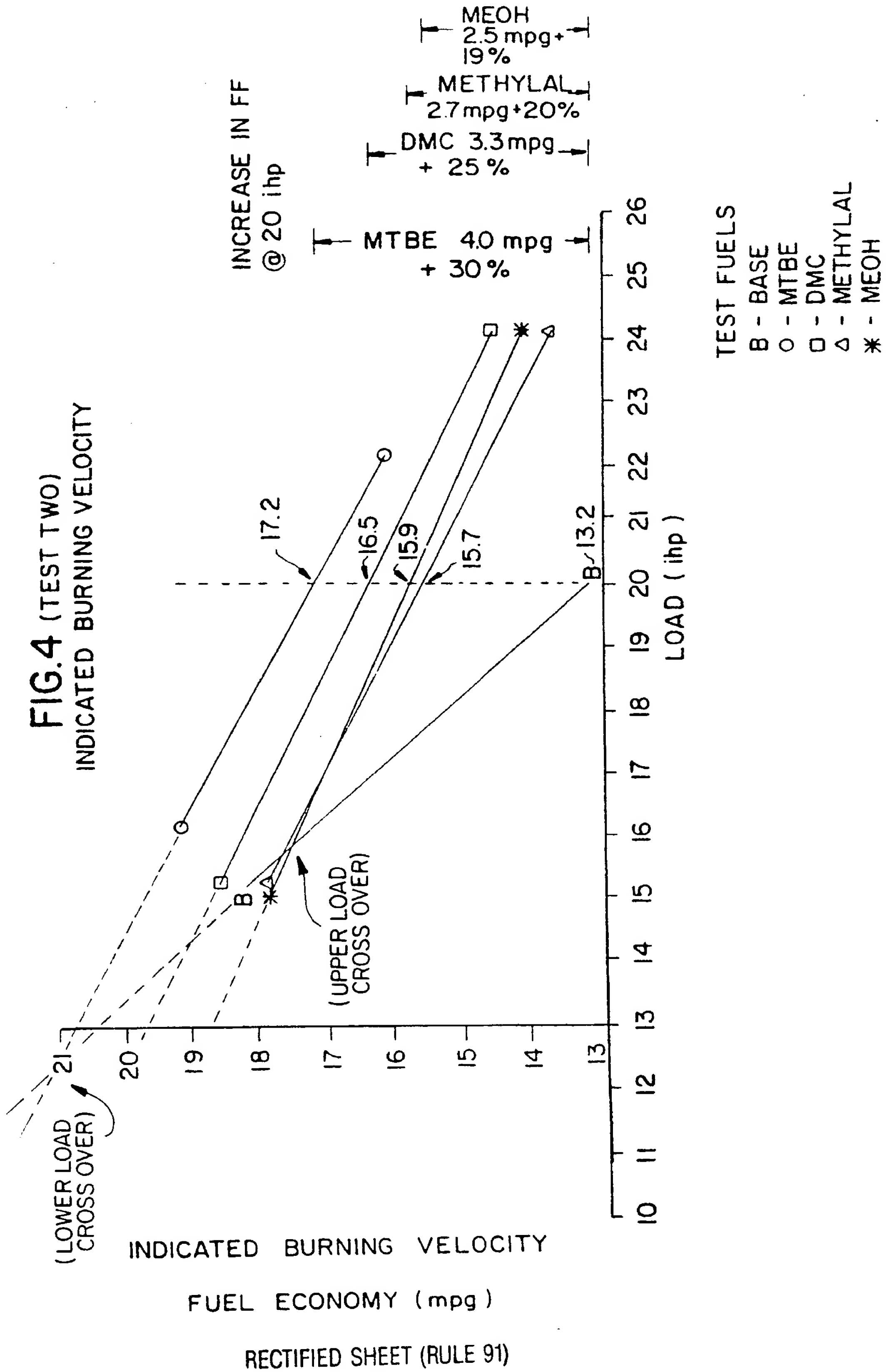


FIG.5(TEST TWO)  
BURNING VELOCITY AND HC EMISSIONS

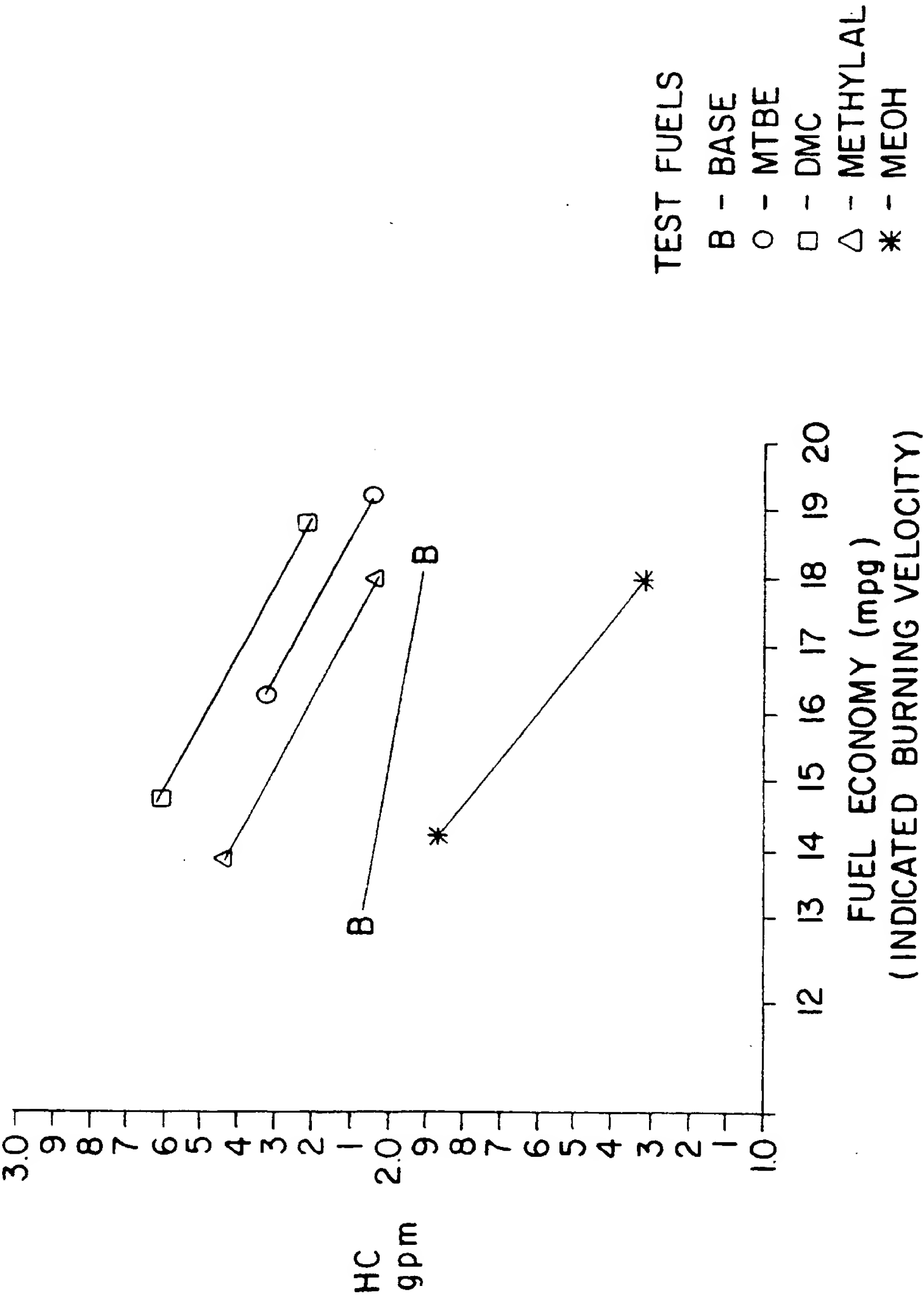
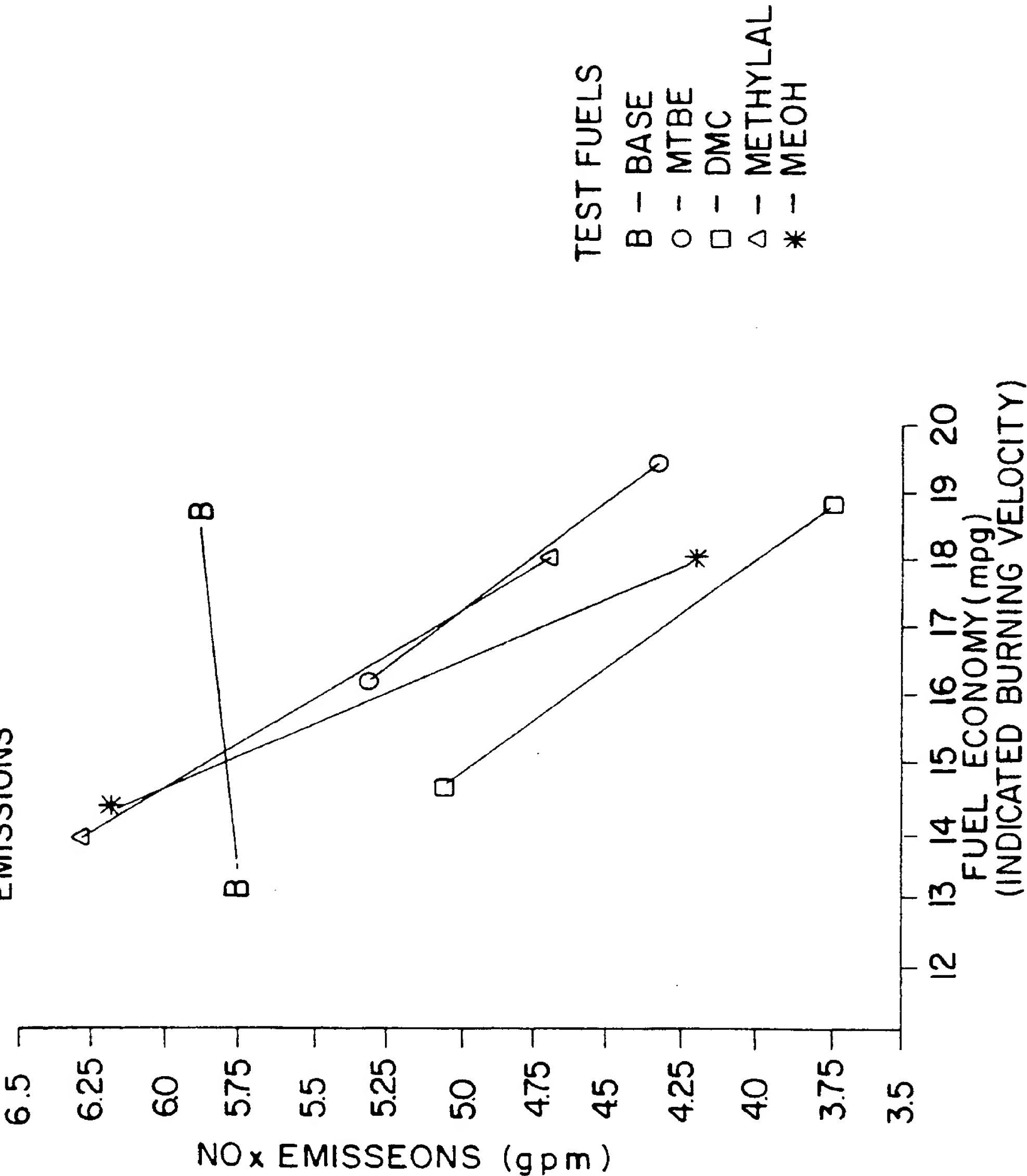
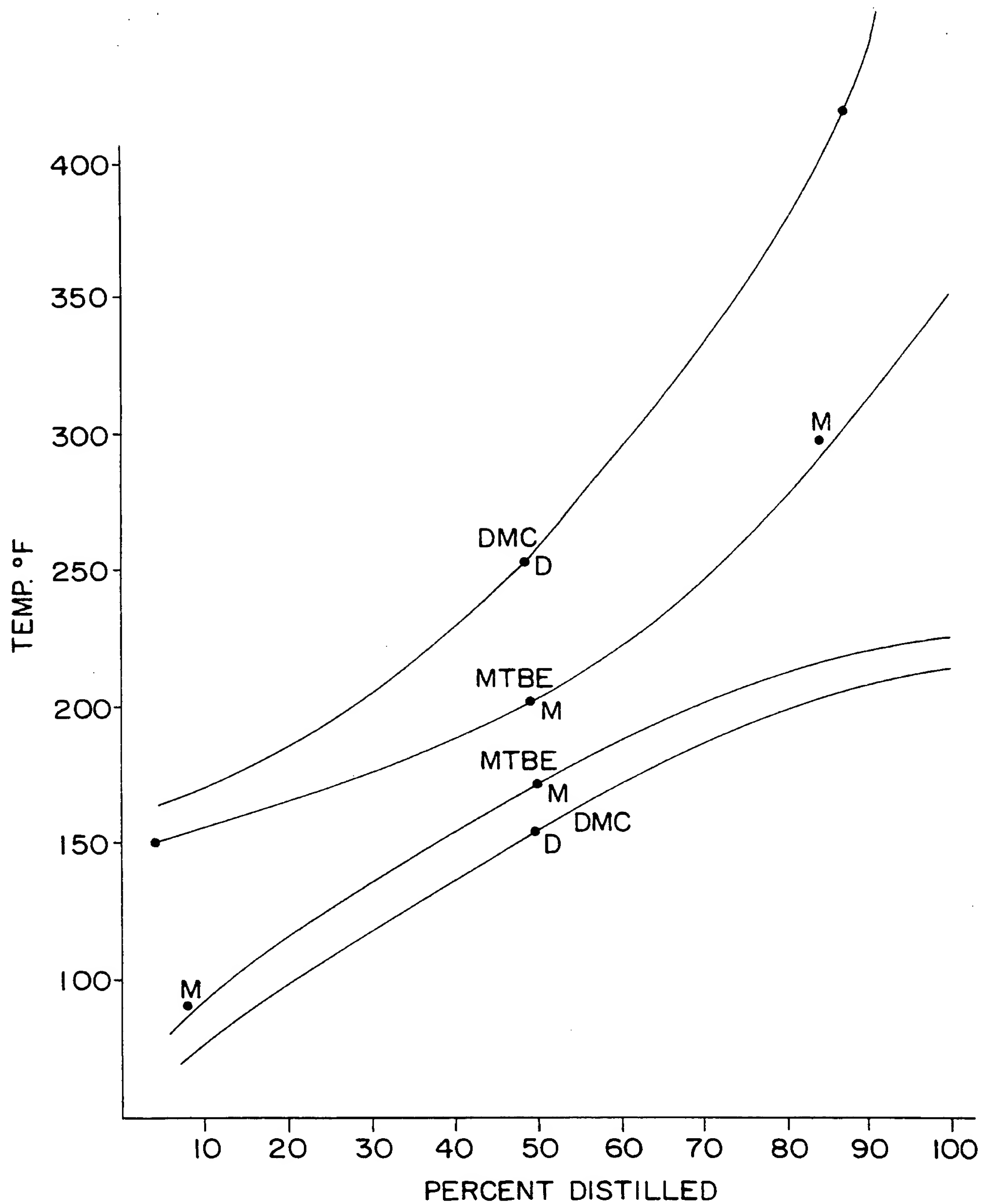




FIG.6 (TEST TWO)  
BURNING VELOCITY AND NO<sub>x</sub>  
EMISSIONS



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FIG. 7

RECTIFIED SHEET (RULE 91)

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/02691

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/30, 1/18

US CL : 44/354, 359, 447, 448, 449

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/354, 359, 447, 448, 449

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,030,195 (Ewan) 17 April 1962, column 1, lines 14-25.	1-15, 19 and 24-26
Y	US, A, 3,224,848, (Henderson) 21 December 1965, see entire document.	1-15, 19 and 24-26
Y	US, A, 3,346,648, (Worrel) 10 October 1967, column 1, lines 7-11; column 16, lines 48-54.	1-15, 19 and 24-26
Y	US, A, 3,976,437, (Shang et al.) 24 August 1976, see entire document.	1-15, 19 and 24-26
Y	US, A, 4,207,078, (Sweeney et al.) 10 June 1980, see entire document.	1-5, 19 and 24-26
Y	US, A, 4,244,704, (Sweeney et al.) 13 January 1981, see entire document.	1-15, 19 and 24-26

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

22 JUNE 1995

Date of mailing of the international search report

01 AUG 1995

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/02691

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,468,233 (Bruderreck et al.) 28 August 1984, see entire document.	1-15, 19 and 24-26
Y	US, A, 4,674, 447, (Davis) 23 June 1987, see entire document.	1-15, 19 and 24-26
Y	US, A, 4,812,146 (Jessup) 14 March 1989, column 1, lines 34-39; column 2, lines 59-64.	1-15, 19 and 24-26
Y	US, A, 5,013,329 (Bell et al.) 07 May 1991, see entire document	1-15, 19 and 24-26
Y	US, A, 5,113,803 (Hollrah et al.) 19 May 1992, see entire document.	1-15, 19, 24-26
Y	US, A, 4,270,929 (Dang Vu et al.) 02 June 1981, see entire document	1-15, 19 and 24-26

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/02691

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1-15, 19 and 24-26

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1-15, 19 and 24-26, drawn to a composition of matter and method of use of said composition of matter.
- II. Claims 16-18, drawn to a method of making a gasoline composition.
- III. Claims 20-22, drawn to a method of increasing the fuel economy of a vehicle.
- IV. Claim 23, drawn to a method of avoiding catalyst exhaust plugging.

The inventions listed as Groups I-IV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I relates to a composition and the use thereof containing an ECS compound and a fuel soluble metallic compound.

Group II relates to a method of making a gasoline composition having a higher latent heat of vaporization.

Group III relates to a method of increasing the fuel economy of a vehicle by reducing the gasoline boiling temperature and adding MMT in an amount up to 1/32 gr mn/gal.

Group IV relates to a method of avoiding catalyst exhaust plugging wherein the fuels exhaust temperatures are reduced and vented into an exhaust catalyst at less than 1400°F.

Additionally, this application contains claims directed to more than one species of the generic invention. The different components under "ECS compounds" (claims 1, 19 and 23) must be members of a recognized class of compounds. The "ECS compounds" are not members of a recognized class of compounds, but, in fact represent a plurality of classes as listed below. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be examined, the appropriate additional examination fees must be paid. The species of ECS compounds, as set forth in the specification at pages 29-32 are as follows:

- a) ethersm) nitrogen oxides
- b) organic carbonatesn) oxides, including ozone
- c) alcohols, glycolso) hydrogen
- d) organic nitro compoundsp) boranes
- e) esters and diestersq) borohydrides
- f) aldehydes and ketonesr) perchlorates
- g) aminess) sulfur compounds
- h) carboxylic acidst) metal hydrides
- i) peroxidesu) water
- j) heterocyclic nitrogen compoundsv) carbon oxides
- k) saturated or unsaturated  
or aromatic hydrocarbons
- l) nitrates

A second component containing species which are not members of a recognized class of compounds, but, in fact represent a plurality of classes are the "fuel soluble metallic compounds" (claim 1) listed below.

- i) metals (organometallic compounds)
  - ii) non-metallic compounds
  - iii) halogen compounds
- Further, the "co-fuel" (claims 3 and 10) represents at least the following classes:

- 1) liquid hydrocarbon fuels
- 2) gaseous hydrocarbon fuels
- 3) solid hydrocarbon fuels
- 4) non-hydrocarbon fuels

Inasmuch as the PCT rules require the International Search Report to be established on the first claimed invention in claim 1, this is determined to be: an "ether" ECS compound with a metallic fuel soluble compound with or without a co-fuel of a liquid hydrocarbon. Additional inventions will be searched if paid for. If less than all additional inventions are to be searched, applicant may specify which inventions are to be searched by identifying them according to the above terms.

The number of additional inventions is calculated as 22 ECS species multiplied by 3 metallic compounds further

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/02691

multiplied by 4 types of fuels for Group I and 22 ECS species for Group IV. Groups II and III relate to a single species. The total number of additional inventions found is therefore 288.

